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H. A. J. BATTAERD AND G. W. TREGEAR

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INTRODUCTION TO THE SERIES

This series was initiated to permit the review of a field of current interest to polymer chemists and physicists *while* the field was still in a state of development. Each author is encouraged to speculate, to present his own opinions and theories, and, in general, to give his work a more "personal flavor" than is customary in the usual reference book or review article. Whenever background material was required to explain a new development in the light of existing and well-known data, the authors have included them, and, as a result, some of the volumes are lengthier than one would expect of a "review."

We hope that the books in this series will generate as much new research as they attempt to review.

H. F. MARK
E. H. IMMERGUT

PREFACE

This book contains information collected by the authors in preparation for a long-term research project on graft copolymers. It was written in an industrial environment and is therefore biased toward the applied rather than the academic side of the subject.

Before embarking on an industrial research project, a number of managerial and technical questions have to be answered, connected with the economic viability of the goals set. This, in turn, requires a careful analysis not only of the general literature but of the patent literature as well. Some statistics on the rate of patenting and by whom, and on what subjects are imperative to predict future competition and select the most likely area for projected activities. These statistics have been included in the appendixes. A further analysis of the main processes and products claimed in relation to priority dates has been added. This was needed to judge which methods, when used, may lead to valid patenting.

The general literature is also discussed with a utilitarian approach. One would like to know the limits of the present knowledge and how much academic endeavor will be required to critically evaluate products and processes. This is particularly important since the strength of a patent is quite often determined by the definition of the products claimed in terms of evaluation.

The authors have attempted to bring all data together in a form of a reference text suitable and useful for the industrial and academic researcher, which can be used for the purpose of gaining a broad impression of the place of graft copolymers in polymer science technology as well as for giving detailed information and references to many thousands of polymers and preparative methods. The authors also admit to a bias toward radiation chemical processes. For the patent literature in particular these have not been reviewed in detail in other texts available on graft copolymers and this book may therefore be of use to those interested in this aspect of graft copolymerization.

The authors wish to express their sincere appreciation to the many people who have assisted in the preparation of this volume.

HANS BATTAERD
GEOFFREY W. TREGEAR

March 1967

Imperial Chemical Industries of Australia and New Zealand Limited,
Central Research Laboratories,
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PART I

GENERAL LITERATURE

I. INTRODUCTION*

1. GENERAL

This book reviews the general and patent literature of graft copolymers to the end of 1965. It appeared opportune to undertake this task in view of the accelerating effort on graft copolymers from industrial origin.

The review is presented in two parts dealing with the general and patent literature, respectively. The magnitude of the research effort can be judged from the fact that some thousand literature references and 1200 patents were found. Over 1500 patented graft copolymers were alphabetically indexed in Part II. The more general information is dealt with in Part I. References are listed at the end of each chapter and an alphabetical index of authors has also been included.

Graft copolymers are slowly finding industrial application. This progress, however, has not been commensurate with the research effort recorded in this volume. Although three monographs are already available (1–3) as well as some 35 review papers (4–38), a detailed review of this type was considered justified on the grounds that scanning of available literature left several important questions unanswered, e.g.:

1. Why, in such an active field, have so few products attained commercial exploitation? What are the technical difficulties?

2. Why should one look at graft copolymers per se, since there are already such an enormous number of degrees of freedom available in random copolymers?

3. What are the physical properties of graft copolymers that cannot be attained by a blend of the corresponding homopolymers?

It was found that the bulk of the information available sadly neglected structural aspects (with the possible exception of fiber grafting) of such great importance in homopolymers and random copolymers, but even more so in complex systems. The field of graft and block copolymers is pervaded with this vague approach to essential structural analysis and definition.

The physical properties of graft copolymers are as yet not fully understood and relatively little information is available. No coherent plan has

---

*** References for this section will be found on pages 8 and 9.**

been developed to allow the test of a systematic approach against experimental results. In the 38 reviews noted (1–38), authors are either optimistic and claim the field of graft copolymers to be a panacea for tailor-made polymers, or bluntly state that grafts behave as the blend of the corresponding homopolymers and therefore are not a particularly exciting exercise. For the few cases in which physical properties are mentioned in the patent literature, claims are often made for the products which in the experience of the authors (39) are of little real value. This situation is possibly accentuated by the difficulty in characterization of grafts which can only be carried through in exceptional cases.

Ceresa (2) discusses only qualified examples of physical properties for two types of polymers; natural rubber/methyl methacrylate grafts (marketed as Hevea Plus MG) and some poly(butadiene-*g*-styrene) with variations. It is noteworthy that both these examples received commercial exploitation.

Burlant and Hoffman (3) devote even less space to physical properties. Sadron (40) recently emphasized this dearth of information at the Canadian Polymer Forum in 1964. He reasoned that the lack of fundamental understanding of properties of graft copolymers is due in part to the fact that the physical state of graft copolymers is more sensitive to the history of formation than is the case for the corresponding homopolymers.

In this book an attempt has been made, at least in part, to supply a rational approach to the problems discussed above. Special attention has been paid to methods using irradiation for the formation of graft copolymers. The large body of information on radiation synthesis has been tabulated alphabetically under the name of the polymer. In Part II a similar classification for synthetic methods using radiation in the patent literature is provided stating, where known, the relation in time between publication in the general literature and the priority date of the first patent. Industrially, the importance of radiation synthesis is reflected by the fact that 24% of all patents dealing with graft copolymers claim a radiation-induced synthesis. In the general literature this proportion is even larger. The question of industrial realization has not yet been resolved, but the authors' bias toward radiation chemistry is founded on the ease of the laboratory preparation of grafts in this manner.

A large body of information on the formation of grafts on natural and synthetic fibers, including some commercial applications, has accumulated in the last three years. Thus the grafting on cellulosic fibers, nylons, polyesters, etc., would fill another volume and consequently was not reviewed exhaustively. This decision was based on the following considerations:

(*1*) the grafting on fibers appeared to be aimed mainly toward surface modification rather than graft copolymers per se, and consequently should be discussed in works on textile treatment, finishing, and dyeing; (*2*) a large proportion of this literature appeared in Japanese and similar "hard-to-translate" languages and could not be reviewed without an extraordinary expenditure in time and money.

A chapter has been included, however, discussing the more fundamental advances in this field, including extensive tabulation of literature. The treatment afforded to fiber grafts is adequate for orientation of those coming from textile interests. Synthetic methods were included in the general discussion on this subject without differentiating between fibers, films, or other forms of the backbone polymer.

Similarly, this distinction has not been made either in the subject index or patent index. For example, grafts on cotton, nylon, yarn, etc., will be found under the generic name of the base polymer in the nomenclature set out in the following chapters.

2. HISTORICAL

Houtz and Adkins (41) provided the first indication that a polymer molecule, in the presence of growing polymer chains, may be capable of increasing its molecular size. Viscosity measurements of the product produced by polymerizing styrene in the presence of polystyrene led them to conclude that the new styrene units were in fact attached to the original polystyrene backbone. These facts were later substantiated on theoretical grounds by Flory (42) who proposed a theory suggesting that branched vinyl polymers could result from chain transfer reactions involving polymer molecules and growing polymer chains.

A few years later Le Bras and Compagnon (43,46) reported interesting properties of a modified rubber prepared by polymerizing acrylonitrile in the presence of a natural rubber latex. The authors could not explain the changes which the rubber underwent from a study of mixtures of acrylonitrile and rubber or by the action of catalysts alone and suggested that it was highly probable that the changes were due to the formation of a compound of the rubber and acrylonitrile.

It became apparent to Carlin and Shakespeare (44) that growing polymer chains should undergo chain transfer not only with polymer molecules composed of the same monomer units but also with polymer molecules composed of different monomer units. Branched chains should then be formed in which the principal chain is composed of one kind and the branch units of another kind. By polymerizing *p*-chlorostyrene in the presence of polymethyl acrylate and examining the solution properties of the product (48) Carlin was able to verify this principle.

At about this time Russian activity in the field became apparent with the publication of several patents by Berlin (45) covering the products formed by polymerizing monomers in the presence of preformed polymers. Up to this stage the concept "graft copolymer" had not been introduced and it was not until 1950 that Alfrey and Bandel (47) in reporting the polymerization of vinyl acetate in the presence of copolymers of styrene and vinylidene chloride and in a later review by Mark (49) that the term "graft" was adopted. The name "graft copolymer" was officially defined in 1952 by the International Union of Pure and Applied Chemistry.

While Carlin and co-workers had demonstrated that branched chains of a polymerized monomer could be attached to a polymeric backbone of different type it was not until the work of Roland and Richards (50) that information as to the points of attachment was obtained. These authors polymerized ethylene in the presence of polyvinyl acetate. Methanolysis of the modified polymer and separation of the resulting fragment showed the different points at which the polyethylene branches had grown on the polyvinyl acetate.

Significant interest in grafting reactions did not develop until the general availability of high-energy radiation. The use of radiation in the synthesis of graft copolymers was first introduced at a Symposium on Macromolecular Chemistry of the International Union of Pure and Applied Chemistry in Milan, Italy, September 1954 by Mesrobian and co-workers (51). Since this time interest in graft copolymers in both industrial and academic circles has developed rapidly as is evident from the vast literature at present available. An attempt has been made in this volume to review a majority of this literature.

3. USE OF TABLES AND APPENDIXES

This book has been written in two parts: Part I covers the general literature, Part II the patent literature. Author and Subject Indexes appear at the end of the book.

1. Part I:

The following tables should be consulted for special information:

Table II. Alphabetical list of graft copolymers made by irradiation techniques.

1a. Polymers prepared by the direct method.
1b. Direct vapor phase grafting.
2. Preirradiation in air.
3. Preirradiation *in vacuo*.
4. Intercrosslinking.
5. Emulsion techniques.

Table IV. References covering the physical properties of graft copolymers arranged in chronological order.

Table XII. References covering the physical properties of cellulose-based grafted fibers in chronological order.

Table XIII. References covering the physical properties of synthetic fiber grafts in chronological order.

2. Part II:

The body of this section contains a list of patent abstracts arranged in order of application date and have been numbered chronologically.

Appendix II. All patents of which the application date could be found.

Appendix III. Some early foreign patents for which the application date was not readily available.

Entry into these tables can be made in several ways:

1. Country of origin and patent number are known. Appendix I relates these to the reference numbers of the abstract.

2. Application date is known. Appendix II is chronological in this respect.

3. Radiation methods. Appendix VI relates the methods utilizing ionizing radiation for the synthesis of graft copolymers to the numbers in Appendix II.

4. Appendix VII lists the references to methods other than radiation for the synthesis of graft copolymers.

5. Polymer is known. Appendix VIII contains an index of the graft copolymers claimed in the patent abstracts of Appendixes II and III. The index has been divided into three parts.

Appendix VIIIa lists alphabetically graft copolymers for which both the polymer backbone and grafted side chain have been specifically defined.

The following coding has been used throughout the index detailed in Appendixes VIIIa, VIIIb, and VIIIc:

(h), e.g., poly(ethylene(h)-*g*-styrene)

The small "h" in parentheses following a monomeric unit indicates that homologs of the series may also be claimed.

*, e.g., poly(butadiene *-*g*-styrene)

The asterisk signifies that *minor* amounts of a copolymer of butadiene may also be claimed as the backbone polymer.

(sub), e.g., poly(vinyl chloride-*g*-acrylamide(sub))

The abbreviation "sub" in parentheses following a monomeric unit signifies that substituted products of that monomer may also be covered by the claim.

C_{2-18}, e.g., poly(styrene-*g*-alkyl acrylate C_{2-18}).

The abbreviation C_{2-18} signifies that the alkyl chain of the acrylate unit may contain from 2 to 18 carbon atoms.

The use of this form of nomenclature was found necessary due to the limited amount of information that could be obtained from a short abstract. In most cases time did not permit an examination of the complete specification.

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II. STRUCTURE AND NOMENCLATURE*

1. STRUCTURE

In the Report on Nomenclature in the field of macromolecules by the International Union of Pure and Applied Chemistry (1,2) graft copolymers are defined in the following words:

> **A graft copolymer is a high polymer, the molecules of which consist of two or more polymeric parts, of different composition, chemically united together. A graft copolymer may be produced, for example, by polymerizing a given kind of monomer with subsequent polymerization of another kind of monomer onto the product of the first polymerization. The union of two different polymers by chemical reaction between their molecular end groups or by a reaction producing crosslinks between the different materials would also produce a graft copolymer.**

This definition takes in various kinds of nonrandom copolymers and it is significant that "block" copolymers are not mentioned in the Union's report. Later work has produced the need to classify these nonrandom copolymers more closely. Allen and other workers (3), for example, define the term as follows:

> **The term "block" copolymer is not standard. We use it to describe linear molecules, whereas branched structures arising from the attachment of side chains of one type of monomer unit on to a backbone of the other types, we call graft copolymers.**

The first significant attempt to classify and code block and graft copolymers was made by Ceresa (4) in a listing of some 2000 polymer systems known in 1961. Since the body of this review contains a similar classification up to 1966, with a considerable increase in the number and complexity of systems recorded, Ceresa's system was adopted and the following description of copolymer structures is based on (4). This nomenclature has also been adopted in the *Encyclopedia of Polymer Science and Technology* (6).

The following models are used to illustrate the various types of polymers where A, B, etc., represent monomeric units such as $—CH_2—CHCl—$ (vinyl chloride) or $—CH(CH_3)—CH_2—$ (propylene).

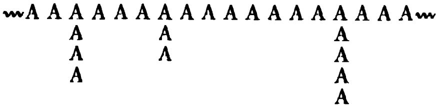
Branching of polymers is accepted as an established fact and long- and short-chain branches and subbranches are not indicated unless strictly necessary. Thus a polymer chain indicated as

$$\sim\!\mathrm{A\ A\ A\ A\ A\ A\ A\ A\ A\ A\ A\ A\ A\ A}\!\sim \qquad (1)$$

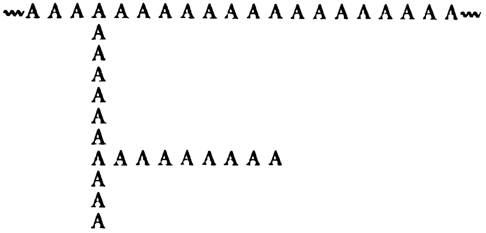
---

* References for this section will be found on page 16.

may contain the long and short branches illustrated in 1a and 1b.



(1a)



(1b)

The simplest case of the *random* copolymerization of two monomers A and B can be represented by

∿A A B A B B B A B A A B A B B A B A A A B A B∿ (2)

For polymers prepared by a one-stage synthesis the two types of monomer units are presented in random arrangements in the polymer chains, since the compositions are governed by the monomer reactivity ratios and the molar concentrations of the monomers. If one of the monomers, A, is not capable of entering into homopolymerization reactions, i.e., radical A will not add to monomer A, then the resulting copolymer would have a structure typified by

∿B B A B A B B A B B B A B A B A B B A B A B B A B∿ (3)

e.g., the copolymerization of maleic anhydride (A) with styrene (B).

Under certain circumstances an alternating copolymer with the structure

∿A B A B A B A B A B A B A B A B A B A B A B A B A∿ (4)

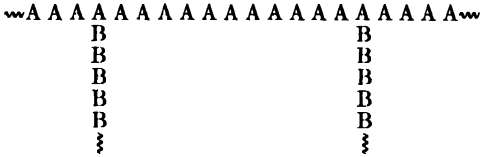
may be formed as in the copolymerization of maleic anhydride and allyl acetate.

The illustrations above have been restricted to simple binary systems, but higher order systems of considerable complexity in number of monomer units and order do exist in synthetic as well as in natural polymers.

Using the same system a "linear *block* copolymer" can be represented by

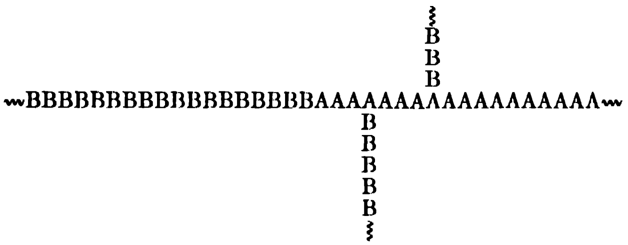
∿A A A A A A A A A A B B B B B B B B B B B B A A A A A∿ (5)

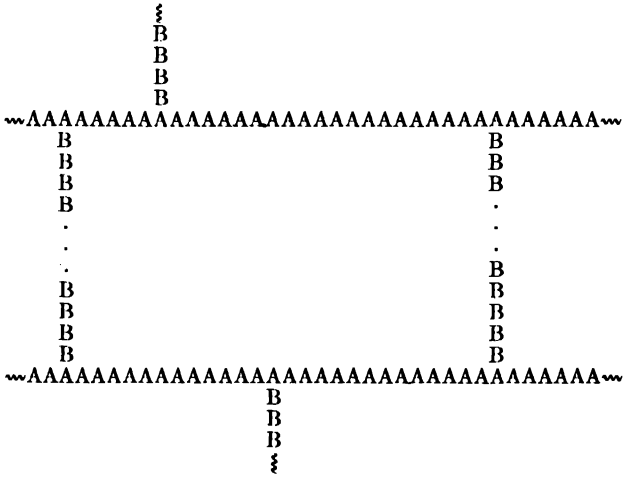
and a "*grafted* block copolymer" by


(6)

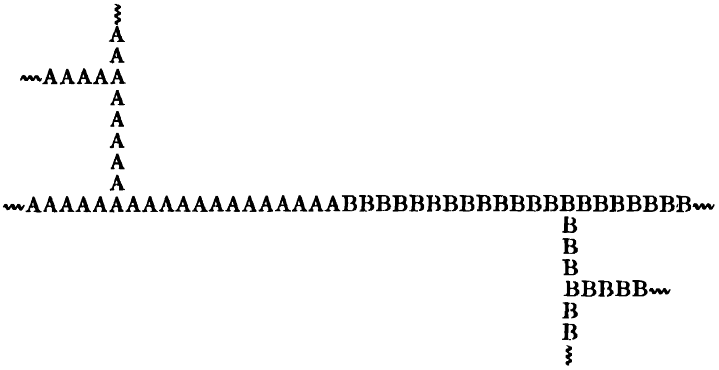
These two main classes of "sequence copolymers" will be referred to in this book as "block" and "graft" copolymers, respectively.

Due to the various methods of preparation, or possible mechanisms involved, the following types must also receive classification:


(7)


(8)

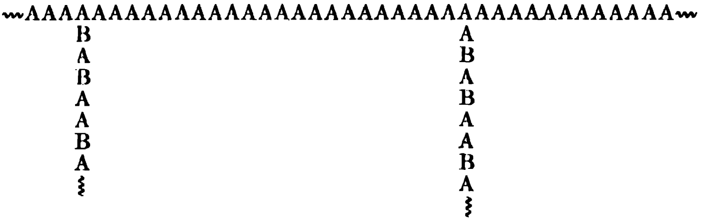
Further subclassification becomes necessary when we consider the composition of the segments of the block or graft copolymer, for these may be homopolymeric or copolymeric, and if copolymeric, alternating or random. Thus, confining ourselves to the two main subdivisions and to random copolymerization within the segments only, it is possible to differentiate between eight additional types of structures for block and graft copolymers of two monomers A and B.



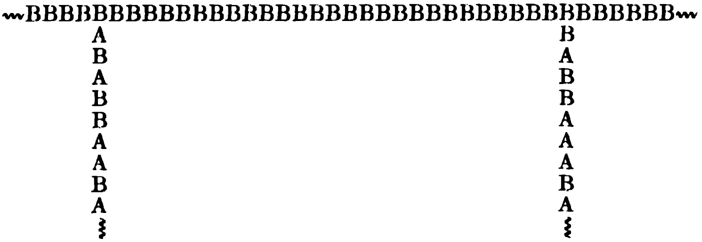
(9)

∼AAAAAAAAAAAAAAAAAABABBABBAABBABABBBBA∼ (10)

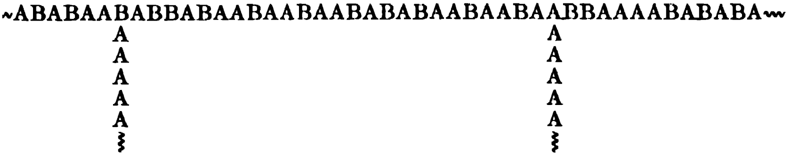
∼BBBBBBBBBBBBBBBBBBBABABAABBABBAAABABAB∼ (11)



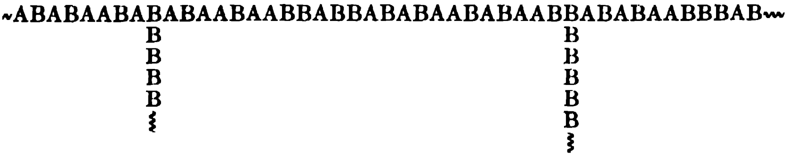
(12)



(13)

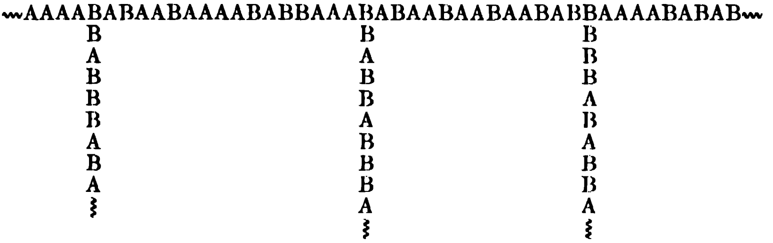


(14)



(15)

$$\sim(\mathrm{AAABAABAAABABAAAABABA})(\mathrm{BBBABBABAABBBABBABBB})\sim \qquad (16)^*$$



$$\sim\mathrm{AAAA}\begin{array}[t]{c}\mathrm{B}\\ \mathrm{B}\\ \mathrm{A}\\ \mathrm{B}\\ \mathrm{B}\\ \mathrm{B}\\ \mathrm{A}\\ \mathrm{B}\\ \mathrm{A}\\ \wr\end{array}\mathrm{ABAABAAAABABBAAA}\begin{array}[t]{c}\mathrm{B}\\ \mathrm{B}\\ \mathrm{A}\\ \mathrm{B}\\ \mathrm{B}\\ \mathrm{A}\\ \mathrm{B}\\ \mathrm{B}\\ \mathrm{B}\\ \mathrm{A}\\ \wr\end{array}\mathrm{ABAABAABAABAB}\begin{array}[t]{c}\mathrm{B}\\ \mathrm{B}\\ \mathrm{B}\\ \mathrm{B}\\ \mathrm{A}\\ \mathrm{B}\\ \mathrm{A}\\ \mathrm{B}\\ \mathrm{B}\\ \mathrm{A}\\ \wr\end{array}\mathrm{AAAABABAB}\sim \qquad (17)^*$$

Since Natta introduced the concept of tacticity in 1958, several block and graft copolymers have been prepared having tacticity in the backbone, in the block or graft chain, or both. Thus to the classifications 1–17 above, variations of the backbone graft and block chains containing atactic, isotactic, and syndiotactic arrangements should be added where applicable.

2. NOMENCLATURE

In the system of nomenclature devised by Ceresa, the major classification is directly derived from the Chemical Abstracts Nomenclature for Homopolymers but is adapted further to include all of the possible variations mentioned above. Thus a homopolymer is written as poly(methyl methacrylate), poly(styrene), poly(vinyl acetate), etc. Random copolymers are indicated by the prefix *-co-*, e.g., poly(butadiene-*co*-styrene) and poly(vinyl chloride-*co*-vinyl acetate). Alternating copolymers are indicated by replacing *-co-* by *-alt-* as in poly(ethylene-*alt*-carbon monoxide). To differentiate between block and graft copolymers it is necessary to introduce two additional prefixes, *-b-* for linear block copolymers segments and *-g-* for grafted block copolymer segments.

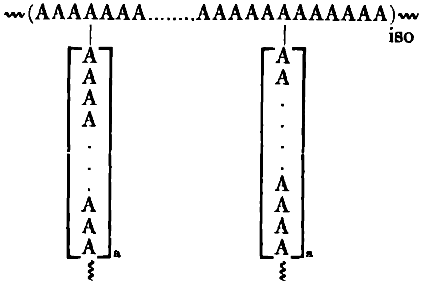
In this nomenclature the first polymer segment named corresponds to the homopolymer or copolymer which is prepared in the first stage of the synthesis. (For grafts this is of necessity the backbone polymer or copolymer.) The following exemplify the classification system: poly(styrene-*b*-methyl methacrylate), poly(methyl methacrylate-*b*-styrene), poly(ethylene-*g*-acrylonitrile), poly(styrene-*g*-butadiene-*co*-styrene), poly([butadiene-*co*-styrene]-*g*-[styrene-*co*-butadiene]). If the convention is accepted that, in a copolymer, the first mentioned monomer is present in the copolymer in the greater proportion, then the last example represents a high styrene–butadiene copolymer grafted on to a low styrene–butadiene rubber.

***Block and graft copolymers with two comonomers with different ratios in the backbone and block or graft chain.**

Conventional prefixes to indicate diene structures can be inserted in their normal positions, e.g., natural *cis*-1,4 poly(isoprene-*g*-methyl methacrylate) (Hevea Plus). The phenomena of branching and crosslinking can likewise be accommodated by using the prefixes [*br*] and [*c.l*], e.g., poly (styrene-*g*-[*br*]-vinylcarbazole), poly([*c.l*] styrene-*g*-acrylonitrile), etc.

Tacticity may be allowed for by using the prefixes suggested by Natta (5) to differentiate between isotacticity [iso], syndiotacticity [syndio], and atacticity [a] as in

$$\sim\underset{\text{iso}}{(\text{AAAA}\ldots\text{AAAAA})}-\underset{\text{syndio}}{(\text{AAAAA}\ldots\text{AAAA})}-\underset{\text{iso}}{(\text{AAAA}\ldots\text{AAAA})}\sim \qquad (18)$$



(19)

If, in the structures 1–19, A signifies styrene and B butadiene, then the nomenclature of the copolymers so typified would be given as:

1. poly(styrene)
2. poly(styrene-*co*-butadiene)
3. poly(butadiene-*co*-styrene)
4. poly(styrene-*alt*-butadiene)
5. poly(styrene-*b*-butadiene)
6. poly(styrene-*g*-butadiene)
7. poly(butadiene-*b*-[styrene-*g*-butadiene])
8. [*c.l.*]poly(styrene-*g*-butadiene)
9. poly([*br*]styrene-*b*-[*br*] butadiene)
10. poly(styrene-*b*-[butadiene-*co*-styrene])
11. poly(butadiene-*b*-[butadiene-*co*-styrene])
12. poly(styrene-*g*-[butadiene-*co*-styrene])
13. poly(butadiene-*g*-[butadiene-*co*-styrene])
14. poly([butadiene-*co*-styrene]-*g*-styrene)
15. poly ([butadiene-*co*-styrene]-*g*-butadiene)
16. poly([styrene-*co*-butadiene]-*b*-[butadiene-*co*-styrene])
17. poly([styrene-*co*-butadiene]-*g*-[butadiene-*co*-styrene])

18. poly([iso]styrene-*b*-[syndio]styrene)
19. poly([iso]styrene-*g*-[a]styrene)

During the development of this nomenclature consideration has only been given to synthetic vinyl and diene homopolymers and copolymers as the block constituents, but condensation or naturally occurring polymers may be included using descriptive or common names where applicable. In naming condensation polymers, it is normal practice to omit the expression "copolymer"; e.g., a phenol-formaldehyde resin (uncured) with poly(methyl methacrylate) is given the nomenclature phenol-formaldehyde-*b*-poly(methyl methacrylate). Other examples are: cellulose-*g*-poly(acrylonitrile), poly(vinyl formal-*g*-phenol-formaldehyde. Nylon (6-6)-*b*-poly(methacrylic acid) and natural rubber-*g*-poly(methyl methacrylate).

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III. SYNTHETIC METHODS

1. RADICAL ATTACK ON MACROMOLECULES*

A. Chain Transfer Reactions

If, in a system containing polymer P and growing chains of monomer M, chain transfer to P (i.e., abstraction of an atom such as H, or halogen, from P) occurs by the growing chains of M units, polymerization of the monomer can take place at these newly formed reactive sites. The product is a graft copolymer. This mode of synthesis was first suggested by Flory (1) in 1937 and it has since been applied in bulk, emulsion, suspension, and solution techniques.

A chain transfer reaction is characterized by a chain transfer constant, representing the ratio of the velocity constant for transfer of the chains to that for their growth. Schultz et al. (2) were the first to determine chain transfer constants during the formation of graft copolymers by polymerization of monomers in the presence of low molecular weight polymers. The role of chain transfer through the polymer is enhanced by a rise in temperature (3,4) since the energy of activation of the chain transfer reaction is greater than that of the growth reaction (5). The rate of chain transfer also depends on the polymer: monomer ratio, the lability of the atom being detached, and the reactivity of the polymer radical (6,7). The type of initiator (8–11) and the concentration used, the chemical nature of the polymer and monomer (which determines their polarity and reactivity), and the presence of steric hindrance are further important factors which influence the efficiency of the grafting reaction.

As the general utility of chain transfer reactions in obtaining graft copolymers is often seriously limited by the reluctance of the backbone to undergo free radical attack, several efforts have been made to synthesize polymers with reactive sites characterized by high transfer constants (12–15). The chain transfer reaction is by far the most common method of synthesizing graft copolymers (16–65), although by its very nature the graft is formed in admixture with homopolymer. The reaction, however, has the advantage of simplicity and is hence widely used.

Considerable confusion occurred in the period 1957–60 over the exact nature of some grafting reactions, and the difference between a chain

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***References for this subsection will be found on pages 45–54.**

transfer reaction and a polymeric radical initiated graft was not always clear. A large number of grafts were prepared by chain transfer reactions, but the mechanisms were elucidated only in comparatively few cases. Allen (8,9), for example, found that the grafting of natural rubber with methyl methacrylate was not, as originally postulated, due to a chain transfer reaction, but to direct initiator attack on the polymer molecule. In an attempt to increase the utility of chain transfer for grafting, several attempts were made to synthesize polymers with reactive sites, characterized by high transfer constants. Fox (12), Gluckman (13), and others gave a theoretical treatment for the case of a polymer with transfer sites in the chain, and verified this theory experimentally using poly(styrene) and poly(methyl methacrylate) with pendant mercapto groups. They reported grafting efficiencies around 80%, compared with 10–20% for unassisted chain transfer. Chaudhuri and Hermans (14) demonstrated similar results for cellulose grafts, by incorporating —SH groups into the cellulose.

A full analysis of all work published in this category is beyond the scope of this volume, but was treated with some detail by Ceresa (2, Ch. I) and Burlant and Hoffman (3, Ch. I). In more recent work (310–324) the distinction between chain transfer and polymeric radical is usually made on the basis of kinetics or initiator choice.

Prabhakara (310), for example, claims a chain transfer mechanism for the grafting of methyl methacrylate on chlorinated poly(isoprene) with benzoyl peroxide. Gesner (311) postulates direct initiator attack on the poly(butadiene) chain, rather than transfer for the grafting of acrylonitrile. Bartl (312) and Natta (324) prefer direct initiator attack on the chain for grafting on poly(ethylene-*co*-vinyl acetate) and poly(ethylene-*co*-propylene) respectively. Serganova (316), Rosenberg (314), and Rao (317) seem to have established chain transfer mechanism, however, for a wide variety of backbones and comonomers.

B. Radical Attack on Unsaturated Polymers

Graft copolymers may be formed when vinyl monomers are polymerized in the presence of macromolecules containing double bonds. As natural and synthetic rubbers are the most typical representatives of polymers containing double bonds in the chain it is not surprising that the majority of the published literature on addition copolymerization techniques deals with "rubber" systems (66–76).

The initiator effect plays an important role in the successful grafting to rubber backbones. Allen and co-workers (75,76) found that good yields of methyl methacrylate–rubber graft copolymers were obtained by the use of benzoyl peroxide initiator, while azobisisobutyronitrile (AZBN) produced only a mixture of homopolymers. The cause of this specific initiator effect, and the mechanism of the graft polymerization was determined by using C^{14}-labeled initiators. It was found that benzoyl peroxide initiated grafting by prior reaction of the derived phenyl and benzoyloxy radicals with the poly(isoprene). This occurred by addition to the double bond and by abstraction of the α-methylenic hydrogen atoms to give poly(isoprenic) alkyl and alkenyl radicals, respectively. The latter then act as loci for methyl methacrylate polymerization. The inability of AZBN to initiate graft polymerization was attributed to the markedly inferior capacity of the resonance stabilized $(CH_3)_2{-}\dot{C}{-}(CN)$ radicals, relative to $C_6H_5\cdot$, and $C_6H_5COO\cdot$, to engage in double bond addition and hydrogen abstraction reactions.

Addition copolymerization of monomers with polymeric systems containing "residual" double bonds has also been employed as a method of graft copolymer synthesis. For example, Smets and Schmets (77) copolymerized small amounts of ethylidene dimethacrylate with methyl methacrylate to form a soluble polymer with pendant unsaturated side groups. Polymerization of styrene or ethyl acrylate in the presence of this unsaturated polymer produced graft copolymers by addition copolymerization.

By reacting cellulose with a mixture of acetyl and methacryl chlorides Berlin and Makarova (78) prepared cellulose acetomethacrylic esters. Methyl methacrylate was then copolymerized into these pendant methacryl groups to give a methyl methacrylate grafted cellulose acetate polymer.

Saigusa and Oda (79) brominated polystyrene with *N*-bromosuccinimide in the presence of benzoyl peroxide and then dehydrobrominated with sodium butoxide to give a polymer with double bonds in the backbone. This unsaturated polymer was copolymerized with vinyl acetate in the presence of benzoyl peroxide both in the mass and in benzene solution to give a mixture of graft copolymers and poly(vinyl acetate).

The addition copolymerization of vinyl monomers across the double bond in unsaturated polyesters has also been shown to yield graft copolymers although of a somewhat complex structure (80–82). Although addition copolymerization reactions take place at lower temperatures and polymer concentrations than those needed for the chain transfer reaction, the process is often complicated by gel formation and chain transfer reactions. Except when the double bonds are in the terminal position (as, for example, with disproportionated polymers) the mechanism may not be clear cut and the reaction often yields grafts with complex structures. This may arise as a cellulose gave disappointing results, and only poor yields of graft copolymer could be obtained (98).

Good examples of this method were given by Rafikov (296), who prepared amber-*g*-poly(styrene) and amber-*g*-poly(methyl methacrylate) by oxidizing amber in air. However, vinyl acetate and acrylonitrile failed to graft on the same material.

Ho (295) prepared poly(styrene hydroperoxide) in emulsion and then grafted styrene and methyl methacrylate. Grafting was confirmed in a number of ways.

Natta (294) prepared poly(propylene-*g*-methyl acrylate) from peroxidized polypropylene and Takemoto (293) oxidized the terminal group of low molecular weight poly(isobutylene) with chromic oxide–acetic acid to ketones, which, after further oxidation with sodium hypobromite, were converted to acid chlorides and grafted to starch to yield starch-*g*-poly (isobutylene). Maksimov (302) treated poly(vinyl alcohol) with maleic dialdehyde, converted the free aldehyde group to hydroperoxides, and subsequently grafted acrylic acid onto the polymer, in the presence of ferrous salts. He claimed that no homopolymer was formed.

2. Ozonization

In a French patent (99) to Polyplastic, published in 1955, Landler and Lebel describe the use of ozone as a method of introducing hydroperoxide groups into natural rubber. Decomposition of the hydroperoxides in the presence of acrylonitrile gave a polymer of improved properties. A few years later the Russian workers Korshak and Mozgova (100) also described the technique. They prepared graft copolymers of poly(ϵ-caprolactam) (100–102), poly(hexamethylene adipamide) (103,104), and poly(ethylene terephthalate) (105), by heating the ozonized polymer in the presence of monomers such as styrene, methyl methacrylate, acrylonitrile, and vinylidene chloride. Kargin, Plate, and co-workers (106,107) extended the process to the grafting of vinyl monomers onto ozonized starch and cellulose.

The method can, in principle, be applied to any polymer containing labile hydrogens or unsaturations and as such offers greater scope than the air oxidation techniques. The extent of ozonization of the backbone polymer, however, can be quite critical and ozonization beyond a certain value can lead to degradation rather than an increase in grafting sites.

Plate et al. (108) attempted to copolymerize styrene to ozonized poly (acrylic acid) and poly(vinyl alcohol) but found that it could only be achieved with the use of a specially designed apparatus.

Kozlov et al. (109,110) investigated the grafting of vinyl acetate to ozonized poly(styrene), acrylic acid to poly(ethylene terephthalate), and styrene to poly(isobutylene). The highest yields were obtained with the acrylic acid poly(ethylene terephthalate) system and the lowest with the vinyl acetate poly(styrene) system.

A detailed investigation of the kinetics and the effects of experimental parameters in the ozonization and subsequent grafting of vinyl monomers to poly(vinyl chloride) was carried out by Landler and Lebel (111). The polymer was ozonized in solution and in the dry state. In the latter case the peroxide content of the polymer initially increased linearly with time of ozonization but leveled off after about two hours. During this period little or no degradation of the macromolecular chain was detected. Similar results were also obtained by the Japanese workers Imoto et al., who investigated the ozonization of starch (112), poly(vinyl chloride) (113), and poly(ethylene) (114) and their subsequent graft polymerization with vinyl monomers.

Interesting results have recently been reported by the Russian workers Plate (115) and Kargin (116), who polymerized styrene in the presence of ozonized isotactic poly(styrene). The graft copolymer formed showed highly elastic deformation between 85 and 235°C and transformation points characteristic for each individual copolymer were detected.

B. Diazotization

Graft polymers can be obtained from polymers containing aromatic amino groups. When such high molecular weight compounds are diazotized a polymeric diazonium salt is formed which reacts with Fe^{2+} to form a polymeric polyradical able to initiate polymerization of vinyl monomers.

$$R\text{—}C_6H_4\text{—}N_2^+ + Fe^{2+} \rightarrow R\text{—}C_6H_4\text{—}\dot{N}_2 + Fe^{3+}$$

$$R\text{—}C_6H_4\text{—}\dot{N}_2 \rightarrow R\text{—}C_6\dot{H}_4 + N_2$$

This reaction was first proposed by Cooper (117) and applied to polymers by Valentine and Chapman (118). The latter authors nitrated polystyrene and reduced and diazotized the nitrated polymer in the presence of a ferrous salt to give polymeric phenyl radicals which were then used to initiate grafting. Hahn and Fischer (119) modified this method by using nitrosyl chloride for the nitrosation of the acetyl–amino derivative from the poly(*p*-aminostyrene). On decomposition these groups furnished active sites for the polymerization of acrylonitrile. Diazonium derivatives of the *p*-aminophenacyl ester of carboxymethyl cellulose and the *p*-aminophenacyl ether of cellulose were synthesized by Richards (120). These cellulose derivatives were used to initiate polymerization of acrylonitrile. In the presence of ferrous sulfate the polymerization proceeded to the formation of a graft copolymer and no polyacrylonitrile homopolymer was detected. Attempts to graft styrene and vinyl acetate on the same derivatives were not successful. Thermal degradation of the diazonium derivatives lead to insolubilization, probably due to crosslinking by combination of free radicals. Moderate success was also obtained in the synthesis of cellulose–poly(*p*-benzamide) graft copolymers by reaction of cellulose derivatives with *p*-aminobenzoyl chloride in the presence of a basic catalyst.

Recently the Russian workers Kryazhev et al. (121) have published data on cellulose–poly(methyl vinylpyridine) graft copolymers prepared free of homopolymer by introducing aromatic NH_2 groups into the cellulose macromolecule. The NH_2 groups were diazotized and decomposed in the presence of a reducing agent and the monomeric 2-methyl-5-vinylpyridine. The latter in the form of its phosphoric acid salt or as the salt of an organic acid in 30–40% aqueous solution (at 60°) gave the highest grafting yields. The average degree of polymerization in the grafts was determined by degrading the cellulose to glucose. The best reducing agents for the diazo groups were found to be thiosulfates, hydrosulfites, and sulfites at elevated temperatures and Fe^{2+} or Cu^{+} salts at room temperature. The presence of sulfite and metabisulfite, however, lead to the formation of homopolymer.

C. Redox Systems

Mino and Kaizerman (122) found that certain ceric salts, such as the nitrate and sulfate, form very effective redox systems in the presence of organic reducing agents such as alcohols, thiols, glycols, aldehydes, and amines. The oxidation and reduction produces cerous ions and transient free radical species capable of initiating vinyl polymerization.

In the case of alcohols (123,124), the reaction can be written as follows:

$$Ce^{4+} + RCH_2OH \rightleftharpoons [\text{ceric–alcohol complex}] \rightarrow Ce^{3+} + H^+ + R\dot{C}HOH \text{ (or } RCH_2O\cdot)$$

If a polymeric reducing agent is employed (poly(vinyl alcohol), for example) and the oxidation conducted in the presence of a vinyl monomer, graft formation will occur. This method of grafting yields substantially pure graft copolymers since the free radicals are formed exclusively on the backbone. By using this technique in both aqueous and emulsion systems Mino and Kaizerman prepared grafts of acrylamide, acrylonitrile, and methyl acrylate to cellulose and other poly(glucosides), poly(galactosides), and poly(vinyl alcohol). Richards and Kimura et al. confirmed the validity of the method by preparing cellulose-*g*-poly(acrylonitrile), cellulose-*g*-

poly(styrene) (125), and starch-*g*-poly(acrylonitrile) (126) virtually free of homopolymer.

Using cerium ammonium nitrate as the redox initiator, the Japanese workers Ide et al. have carried out detailed investigations on the effects of polymerization temperature and variations in catalyst, monomer, and nitric acid concentrations. They had studied and prepared graft copolymers of vinyl acetate (127), methyl methacrylate (128), methyl acrylate, acrylonitrile (129), and styrene (130) to cellulose as well as the grafting of methyl methacrylate to poly(vinyl alcohol) (131).

The effects on the physical properties of paper by ceric ion initiated grafting of acrylonitrile has been reported by Daniel and Moore (132). The grafted paper showed improved resistance to acids and improved wet and dry strength properties and dimensional stability, together with increased stiffness and resistance to abrasion. Similar work has been reported by Schwab et al. (133) who studied the effects of grafting acrylamide, acrylonitrile, and some acrylic and methacrylic esters to paper. Cornell (134) grafted vinyl chloride onto a bleached kraft pulp in amounts up to 60% by using the ceric ion redox system but found that homopolymerization accompanied the grafting in appreciable amounts. Data are present on the refining properties, strength, and moisture sensitivity for a pulp sample with 20% grafted poly(vinyl chloride).

Bergheim et al. (135) have reviewed the methods of grafting monomers onto cellulose and describe their own work on the grafting of acrylic monomers onto wood cellulose by the ceric–redox method. Many other studies on the use of the ceric–redox system have been reported in the literature especially in the grafting of monomers to cellulose backbones (136–140).

Initiating systems other than the ceric ion have been tried by some authors with varying degrees of success. In particular the Russian school of Rogovin et al. favor the use of pentavalent vanadium as the oxidizing agent. They have reported its use in the preparation of dialdehyde cellulose-*g*-poly(acrylonitrile), poly(acrylamide-*g*-2-methyl-5-vinylpyridine), poly(methacrolein-*g*-acrylonitrile) (141), cellulose-*g*-poly(acrylonitrile), cellulose-*g*-poly(2-methyl-5-vinylpyridine), cellulose-*g*-poly(acrylic and methacrylic acids) (142,143), celluose-*g*-poly(methyl methacrylate) (144), and cellulose-*g*-poly(dimethylvinylethynylcarbinol) (145).

A sodium thiosulfate–potassium persulfate redox system has been used by Kulkarni et al. (146) in the preparation of cellulose acrylonitrile graft copolymers. Traces of copper were found to accelerate the rate of polymerization giving higher yields.

Oxidation with sodium periodate has also been used to produce free radicals on a cellulose backbone. In the presence of methyl methacrylate or acrylonitrile graft copolymers have been formed relatively free of homopolymer (147).

More recently redox systems have received detailed attention. Rogovin (276), Krassig and Stannett (280), Livshits (282), and Kao (287) reviewed the field. For details these reviews should be consulted.

Tsuji (271), Kulkarni (272), Neimo (273), Simionescu (274), Iwakura (279), Livshits (281), Negishi (277), and Sun (283) have contributed detailed insight into the ceric–redox system for cellulose grafting, the influence of the structure of the base and reaction conditions. The Fe^{2+}–H_2O_2 system was also studied in considerable detail by Morin (285), Korotkova (284), Gulina (270), and Mal'tseva (275). The pentavalent vanadium system, however, found only one adherent (Singh, 269). Obuchi (288) used the system Ag^+–$S_2O_8^{2-}$ to graft methyl methacrylate to rayon. Singh (289) investigated the general utility of the system manganic sulfate–sulfuric acid for the polymerization of vinyl monomers to cellulose, its derivatives, and poly(vinyl alcohol).

D. Trapped Radicals

If during a free radical polymerization the system becomes highly viscous or crosslinked, then, owing to the lack of mobility of the growing chains, there may be a slowing down in the termination step. Apart from the kinetic features associated with this effect, called the Trommsdorff or gel effect (148,149), due to the non-steady-state conditions which then arise in the system, macroradicals of long lifetime can be formed. These trapped or occluded macroradicals can be used to initiate the polymerization of a second monomer yielding block and graft copolymers.

Using this general technical Shashoua and Van Holde (150) prepared true 100% grafted polymers by a two-stage process. They prepared microgels of styrene crosslinked with divinylbenzene, methyl acrylate crosslinked with divinylbenzene, and acrylonitrile crosslinked with methylene bisacrylamide by an emulsion technique and showed that the system contained long-lived active species capable of initiating the polymerization of vinyl monomers such as styrene and acrylonitrile. Microgels are crosslinked polymer particles of approximately 0.1 μ in size and were first described by Baker (151). They behave as single macromolecules and can be dispersed in solvents to give thermodynamically true solutions called microsols (152). Shashoua and Van Holde analyzed the grafted polymers as microsols by limiting viscosity number and by ultracentrifuge measurements. The results indicated that grafting was best initiated by residual free radicals in the microgels and that 100% grafting efficiency could only be achieved when all competitive modes of initiation were inhibited. The authors were further able to demonstrate the existence of polymeric free radicals of lifetimes greater than 100 days.

Popcorn polymers of polybutadiene also contain trapped radicals. Grafting of these materials with styrene (153) and methyl methacrylate (154) has been reported. An unexplained feature of this grafting reaction is that its rate often increases exponentially with time. Polymerizations initiated by a variety of popcorn polymers have been described by Whitby (155).

3. PHOTOCHEMICAL SYNTHESES*

If a molecule absorbs electromagnetic radiation in the visible and UV region, its energy is momentarily increased and the molecule is said to be in an excited state. This energy-rich molecule can either dissociate into reactive free radicals or dissipate its energy by fluorescence, phosphorescence, or collisional deactivation. For a polymer, the former process can lead to the formation of free radical sites on the polymer backbone which can be used to initiate block and graft copolymerization. If none of the bonds in the polymer are ruptured by the radiation, the process can be promoted by the addition of photosensitizers. Upon absorption of UV or visible energy a photosensitizer itself can decompose into active radicals or can transfer its energy to other molecules in the system, thereby promoting the copolymerization reaction. Aliphatic ketones are useful sensitizers. Their photolysis both in the gas phase and in solution has been shown to occur by two simultaneous reactions (156–158): type I, in which two free radicals are formed,

$$\mathrm{R{-}CO{-}R'} \xrightarrow{h\nu} \mathrm{R\cdot + R'CO\cdot \rightarrow R\cdot + R'\cdot + CO\cdot}$$

and type II, in which the molecules can split in the α–β position to the carbonyl group to give an olefin and a lower ketone, without the formation of free radicals, e.g.,

$$\mathrm{R{-}CH_2{-}CH_2{-}CH_2{-}CO{-}R'} \xrightarrow{h\nu} \mathrm{RCH{=}CH_2 + CH_3COR'}$$

As an extension to this early work it occurred to Guillet and Norrish (159) that vinyl polymers containing carbonyl groups may undergo similar reactions upon irradiation. If this were the case, the macromolecular free radical so formed could be used to initiate block and graft copolymerizations. The authors photolyzed a solution of poly(methyl vinyl ketone) in dioxane in the presence of acrylonitrile, vinyl acetate, and methyl methacrylate (160), and detected a mixture of graft and homopolymers as well as acetaldehyde and methane. On analogy with the earlier work they interpreted the results according to Scheme 1.

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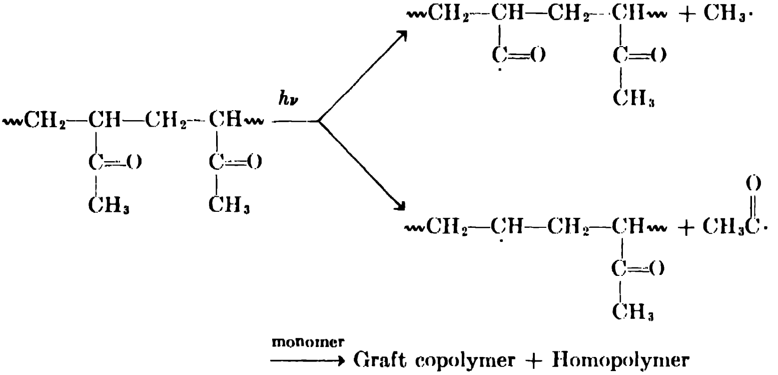
*References for this subsection will be found on pages 45–54.



Scheme 1

In addition to carbonyl groups, carbon–halogen bonds can be incorporated in a polymer as the radiation labile site. Thus Dunn et al. (161,162) polymerized styrene in the presence of carbon tetrabromide and bromotrichloromethane which resulted in a chain containing halogen end groups. Subsequent photolysis of the macroradical in the presence of methyl methacrylate produced block copolymers in addition to homopolymer. Chlorine atoms as side groups on a polymer macromolecule may be photolyzed when they are activated by a second polar grouping. Miller (163,164), prepared copolymers of α-chloroacrylonitrile (1–3 mole %) with acrylonitrile and with acrylamide. These copolymers were sufficiently stable to be handled in solution but when irradiated the chlorine atoms were photolyzed to give free radical grafting sites. Grafting with acrylamide and acrylonitrile is described.

Using chemical methods to introduce bromine atoms at random sites along the polymer chain, Jones (165) prepared poly(styrene-*g*-methyl methacrylate) by irradiating benzene solutions of polystyrene in the presence of the monomer. The molecular weight of the homopolymerized methyl methacrylate was measured after separation from the graft copolymer and good agreement was obtained in comparing this molecular weight to that calculated from kinetic data if it was assumed that the brominated poly(styrene) functioned only as an initiator. The calculations also indicated that on the average from 1.2 to 5.9 branches of poly(methyl methacrylate) were grafted to each poly(styrene) molecule.

By refluxing poly(styrene) in benzene solution with tetraethylthiuram disulfide for 24 hours Otsu (166) was able to introduce photosensitive groups at random positions along the poly(styrene) chain. Photolysis of this polymer in the presence of methyl methacrylate (166) and vinyl acetate (167) gave block and graft copolymers.

Direct photoinitiation can only be applied to a comparatively few polymer systems but by utilizing a photosensitizer this general technique can be extended considerably. Oster and co-workers first applied this modified technique to the grafting of acrylamide onto natural rubber (168). Unvulcanized natural rubber containing benzophenone in contact with an aqueous solution of acrylamide was irradiated with UV light to produce the graft copolymer. In later work the authors investigated the UV-induced crosslinking and grafting of low- and high-density poly(ethylene) (169). Chlorobenzophenone, deoxybenzoin, and 4,4′-dimethylbenzophenone were also found to act as efficient photosensitizers. Further to the work of Oster, Cooper, and Fielden (170,171) reported the graft copolymerization of methyl methacrylate and styrene to natural rubber in emulsion systems. In spite of the fact that a natural rubber latex is opaque to UV light (some 50% of the light is reflected from the surface and the penetration for 90% absorption is less than 0.1 mm) good yields were obtained by the use of 1-chloranthraquinone as sensitizer.

Menon and Kapur (172), modified this method of latex grafting by irradiating the natural rubber latex and vinyl monomer under nitrogen in the presence of water-soluble photosensitizers such as ferric hydroxide and ferric chloride. The mechanism of such photopolymerization has been the subject of a detailed investigation (173,174) and it has been shown that the primary photochemical process involves an electron transfer followed by the dissociation of the primary product to generate a free radical which then initiates the vinyl polymerization. Another procedure consists in the use of hydrazine as the initiator. The mechanism of initiation has been investigated (175) and evidence has been obtained in favor of an initiation reaction involving the hydrazyl radical formed by one-electron oxidation of hydrazine by a metallic ion under the appropriate reaction conditions, e.g.,

$$N_2H_4 + M^{x+} \rightarrow N_2H_3^{\bullet} + M^{(x-1)+} + H^+$$

where M^{x+} represents a one-electron oxidant.

Geacintov, Stannett, and co-workers (176,177) absorbed photosensitive dyes, such as the disodium salt of anthraquinone(2,7-disulfonic acid) into cellulose, cellulose derivatives, and other polymers and photolyzed them in the presence of acrylonitrile, vinyl acetate, styrene, methyl methacrylate, and monomer systems of styrene–acrylonitrile. The photoexcited dye molecule apparently abstracts a hydrogen atom from the substrate thus forming a macroradical capable of initiating the graft copolymerization. The extent of grafting was found to increase with the time of irradiation and the monomer and dye concentration. The grafting was always accompanied by homopolymerization which was not inhibited by atmospheric oxygen. Both grafting and homopolymerization were, however, completely inhibited by bubbling air through the solution. In addition to the production of a backbone free radical by sensitizer attack, the formation of a dye radical was postulated to account for the simultaneous homopolymerization observed. Continuation of polymerization after photolysis was noted in some cases, a phenomenon believed to be due to subsequent reactions of trapped free radicals. Good evidence of grafting was obtained by comparing the solubility characteristics of the graft with those of a physical mixture of the two homopolymers.

It is possible to attach vinylpyrrolidone branches on dextran by chain transfer and irradiation techniques. Dextran, however, is a very poor chain transfer agent with only one or very few transfer sites so that usually a dextran-poly(vinylpyrrolidone) block polymer is produced. Shen and Eirich (178), however, found that grafting by UV radiation in the presence of benzophenone and its derivatives lead to different, more truly grafted forms but the amount of poly(vinylpyrrolidone) was limited and the branches appeared to be very short, probably because of difficulties in attaining access to the growing sites. Allyl cellulose and styrene can similarly be copolymerized by photolysis in the presence of benzoin (179).

Oster and co-workers (180) demonstrated that vinyl compounds could be polymerized by visible light in the presence of dye–reducing agent–oxygen systems. Following on from this work Smets et al. (181) set out to find whether the photosensitizer actually became incorporated in the polymer. From spectrophotometric data the authors were able to show that dyes such as eosin, acridine orange, and safranine are built as leuco derivatives into poly(acrylamide). Further, by use of this incorporation, they were able to prepare block and graft copolymers by attaching eosin molecules either as side or as end groups onto existing polymers. Poly(vinylamine) carrying 10 mole % eosin groups was synthesized from poly(vinylamine) and eosin lactone and the polymer used for initiating the polymerization of acrylamide, acrylic acid, acrylonitrile, and styrene. Ascorbic acid was used as the reducing agent and the reaction system was saturated with oxygen. The method also made possible the synthesis of polymers with branches of different chemical structure by successive photopolymerizations of two different monomers, e.g., acrylamide and acrylic acid. Similarly, starting from ω-*N*(eosin)poly(methyl methacrylate), block copolymers were synthesized with styrene and acrylamide. By hydrolysis experiments it was demonstrated that the leuco dye group constituted the intermediate link between the two monomer sequences in these block polymers.

Graft copolymerization of several vinyl monomers on chlorinated isotactic poly(propylene) initiated by UV light was studied by Ohshika (182). From the IR spectra of the copolymer obtained, methyl methacrylate, acrylamide, vinyl acetate, and styrene were found to be grafted to the chlorinated poly(propylene) but the amount of the grafted polymer was very small except for the methyl methacrylate case. The authors suggest that the graft copolymerization takes place due to a competitive reaction between two different mechanisms: (*1*) grafting on the polymer radica produced by scission of the C Cl bonds, and (*2*) grafting initiated by hydroperoxides formed on the tertiary carbon atoms in the amorphous regions. Besides graft copolymerization, dehydrochlorination, dechlorination, and crosslinking reactions were observed.

The Korean workers Shim and Jun (183) studied the grafting of styrene to poly(vinyl alcohol) by photolysis using benzophenone as sensitizer. In the presence of water added immediately before irradiation, the highest percentage of grafting was 20%. For irradiation times up to 24 hours the amount of grafting was proportional to time and presumably was initiated at the surface. After a certain degree of grafting, a definite maximum was reached.

Increased grafting efficiency in the presence of water was also reported by Guzman and co-workers (184) who studied the photochemical graft copolymerization of methyl methacrylate onto cellulose. The most reactive system was found to be 32.5% methyl methacrylate in acetone–H_2O (12.5:1) with 3.5 g benzoin as sensitizer. Successful grafting was also obtained with butyl methacrylate but styrene and acrylonitrile presented difficulties. The authors discuss probable mechanisms.

Gnip (291,292) quantitatively evaluated the kinetics of the grafting reaction of acrylonitrile on kapron fibers under the influence of UV light, for the liquid and vapor phase. The rate constant for chain growth and termination, as well as activation energies, are given.

4. MECHANICAL DEGRADATION*

When a polymer molecule is subjected to an applied shear or stress, bond scission may take place producing free radicals at the ruptured ends of the chains. If a monomer is present during this process block copolymerization can be initiated. Similarly if a mixture of polymers is subjected to an applied shear, block copolymers are produced by the coupling of the free radicals at the ends of segments derived from the different polymers. In some instances chain transfer may occur resulting in the location of the free radical in a nonterminal position on the polymer chain. Further, as disproportionation is the most usual termination process (except for poly(styrene)), the termination of two radical-containing fragments will yield one polymer chain terminated by a double bond. In both cases copolymerization will lead to grafted structures.

Numerous methods of mechanical degradation of macromolecules and the subsequent formation of block copolymers have been developed and include:

1. The cold mastication, milling, and extrusion of polymers in the viscoelastic state.

2. The comminution and vibromilling of amorphous and crystalline polymers.

3. The ultrasonic irradiation of polymer solutions under cavitation conditions.

4. The high-speed stirring and shaking, and forcing of polymer solutions through narrow orifices.

5. The freezing and thawing of polymer solutions.

6. The swelling of crosslinked or highly entangled polymers in the vapor phase.

7. The discharging of high-voltage sparks through polymer solutions.

Most of the above methods lead predominantly to the formation of block copolymers with grafting arising only in certain cases (as has been indicated above). In this context then, only brief mention will be made of these methods and for a more detailed account of the use of mechanical degradation processes in the synthesis of block copolymers the reader is referred to Ceresa, *Block and Graft Copolymers*, London, Butterworths, 1962, Ch. 5, pp. 65–101.

Cold mastication, milling, and extrusion of polymers in the viscoelastic state have been used widely in the synthesis of block copolymers especially for the natural and synthetic rubber systems. The polymer is generally masticated in the absence of oxygen and in the presence of a polymerizable monomer or in the presence of another polymer. In either case a mixture of block and graft copolymers results, usually referred to as an interpolymer. Extensive studies have been carried out on the mastication of polymer–polymer and polymer–monomer mixtures by Ceresa and co-workers at the British Rubber Producers Research Association (208). The use of mastication processes in the synthesis of block and graft copolymers has also been reviewed by Bateman (185), Baramboim (186), and Watson (187).

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*References for this subsection will be found on pages 45–54.

Intensive mechanical disintegration of solid inorganic substances such as carbon black, graphite, quartz, sodium chloride, magnesium, and iron metals can lead to the formation of specific active centers of an ionic or free radical nature on the freshly formed surfaces (188). These centers can react with monomers causing polymerization (189) or with polymers causing grafting (188). In this way Plate and co-workers were able to graft poly(styrene) onto silicon dioxide and obtain soluble copolymers containing up to 7.0% of bound silicon (190).

Vibromilling of blends of two or more polymers or of a polymer in the presence of a monomer has been shown to yield block copolymers. Grohn and Bischof (191), for example, synthesized poly(methyl methacrylate-*b*-vinyl chloride) by vibromilling poly(methyl methacrylate) in the presence of gaseous vinyl chloride.

The ultrasonic irradiation of polymer solutions under cavitation conditions leads to chain rupture and if the solution contains a monomer or another polymer, block copolymers may be formed. Henglein (192) was the first to apply ultrasonic degradation to the synthesis of block copolymers but the technique has since been used by many other authors (193–199).

Nozaki (200) has shown that block copolymers can be formed by subjecting dilute solutions of polymers dissolved in monomers, or monomer solvent mixtures, to agitation treatments such as high-speed stirring, shaking, or by forcing the solutions repeatedly through narrow orifices. Among the polymers which have been subjected to such a degradation are addition polymers, poly(vinyl chloride), poly(styrene), poly(acrylamide), as well as cellulose derivatives, phenol–formaldehyde linear condensation products, and poly(ethylene terephthalate).

The mechanical degradation of polymer chains during the freezing and thawing of aqueous solutions and emulsions has been utilized to prepare block copolymers of starch and poly(styrene) and starch and poly(acrylonitrile) (201–203).

When solutions of polymers in monomer–solvent mixtures are subjected to high-voltage spark discharges, block copolymerization is initiated by the macroradicals produced by mechanical degradation (202,204,205). Block copolymers of methyl methacrylate with poly(trifluoroethylene) and poly(vinyl chloride) have been prepared by this method (197,206).

The swelling of a polymer in the vapors of a monomer, e.g., the swelling of poly(methyl methacrylate) by acrylonitrile and styrene, of cellulose acetate by acrylonitrile, and of poly(ethylene) by methyl methacrylate and styrene results in the rupture of polymer chains to produce polymeric radicals and resultant block copolymer formation (202,207,208). The rupture of polymer chains by vapor-phase swelling is also thought to be a likely source of polymeric radicals in the diffusion controlled growth of popcorn polymers and this postulate has in fact been put forward to explain some of the anomalous features of popcorn copolymerization (208).

Akiyama (290) recently studied the system poly(ethylene)–acenaphthylene in some detail. Poly(ethylene) roller-milled in air did graft with acenaphthylene; however, the addition of benzoyl peroxide was necessary before grafting took place. Alternatively, poly(ethylene) irradiated before roller-mixing with UV or γ-rays could induce grafting.

5. IONIC SYNTHESIS*

In addition to the more general free radical processes, graft copolymerization has been shown to occur by a purely ionic mechanism. In an anionic mechanism, grafting is initiated by carbanions while carbonium ions are operative in initiating polymerization under cationic conditions.

A. Initiation by Carbonium Ions

Haas, Kamath, and Schuler (209,210) attempted to polymerize various monomers with cationic initiators such as BF_3 and $SnCl_4$ in the presence of polystyrene derivatives in an effort to obtain graft copolymers by an ionic process. No success was achieved in grafting with vinyl butyl ether, vinyl ethyl ether, isobutylene, *N*-vinylpyrrolidone, or pinene under the particular experimental conditions employed; however, when styrene was polymerized in the presence of poly(*p*-methoxystyrene) graft copolymer was readily obtained. The ionic transfer reaction between the polystyrene carbonium ion and backbone polymer may be represented as in Scheme 2.

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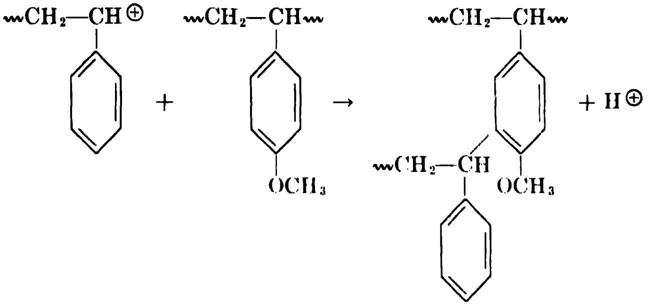
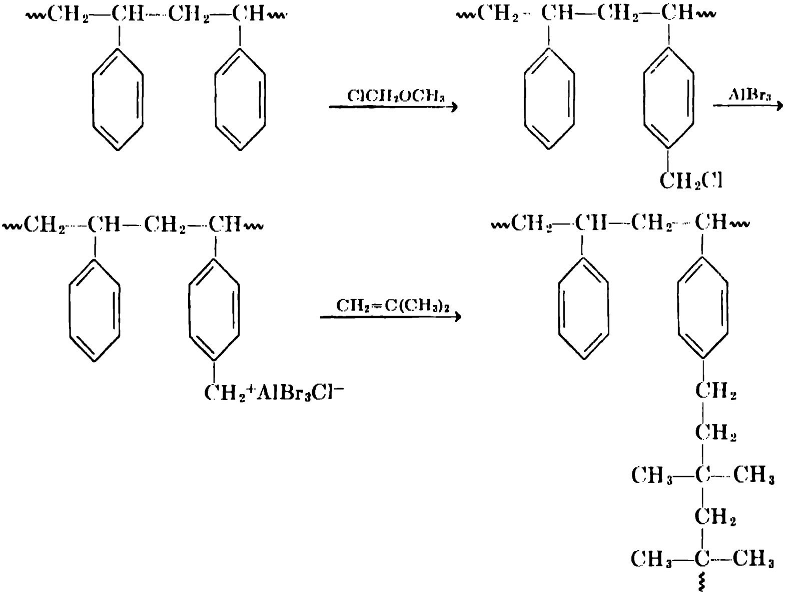
*References for this subsection will be found on pages 45–54.



Scheme 2

It was found that the rate of polymerization of the styrene was independent of the concentration of poly(*p*-methoxystyrene) in the range studied (4.59×10^{-2} to $66.2 \times 10^{-2}M$), but above $38 \times 10^{-2}M$ the styrene ceased to polymerize. The chemical composition of the graft fraction was also found to be independent of the poly(*p*-methoxystyrene) concentration.

Chloromethylated polystyrene in carbon disulfide solution in the presence of aluminum tribromide was used by Kockelbergh and Smets (211) to initiate the polymerization of isobutylene by a carbonium ion mechanism, as in Scheme 3.



Scheme 3

The reaction was carried out at −60°C and the graft copolymer was separated from the benzene mixture by a precipitation technique involving the successive use of methyl ethyl ketone and methanol as precipitating agents. The grafting yields were quite low (5–18%) due possibly to the crosslinking side reactions of the aluminum bromide and the halomethyl poly(styrene).

Plesch (212) treated poly(vinyl chloride) and vinyl chloride–vinylidene chloride copolymers with titanium tetrachloride to initiate the carbonium polymerization of styrene. Indene, *trans* stilbene, and indole were also grafted to poly(vinyl chloride) by the same technique. Plesch found that aluminum chloride also initiated grafting but degradation and discoloration occurred, presumably because of the presence of carbonium ions in the main chain. Teyssie and Smets (213) found that by using the less acidic titanium tetrachloride and working at a low temperature this effect could be eliminated.

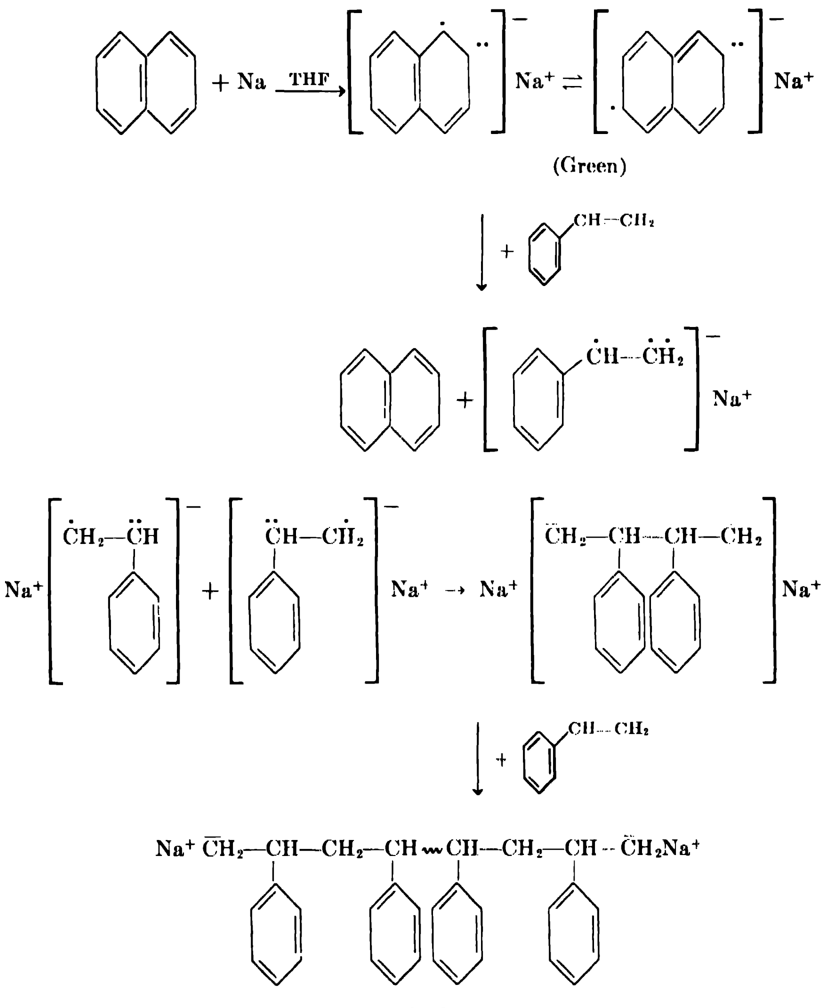
The Japanese workers Rausing and Sunner (214) prepared a cationic catalyst by the adsorption of boron trifluoride onto the surface of cellulose. The interaction of the cellulose hydroxyls and the catalyst yielded reactive sites for the polymerization of isobutylene and α-methylstyrene. These monomers were polymerized on the surface of cellulosic fibers in paper and wallboard at −80°C.

Jaacks (306) produced block and graft copolymers of trioxane, using the reactive C—OC link in poly(vinyl acetate), poly(ethylene terephthalate), poly(1,3-dioxolane), or poly(vinyl butyral) as transfer agents in the cationic polymerization of trioxane.

B. Initiation by Carbanions

The reaction of metallic sodium with an aromatic hydrocarbon such as naphthalene, in the presence of tetrahydrofuran and under moisture-free conditions, yields a green-colored, soluble complex which can initiate polymerization of conjugated olefins via an electron transfer process. Szwarc (215,216) used this complex to initiate the polymerization of styrene at low temperatures. (See Scheme 4.)

He showed that the red polymer solution so formed still contained active polymer chains even when all the monomer had been consumed. If more monomer was added, polymerization continued; hence the polymers were called "living polymers." The addition of a second monomer species, which also polymerized by an anionic mechanism, to the living radicals resulted in the formation of block copolymers, the terminal segments of



Scheme 4

which were, in general, unterminated. If methyl methyacrylate or acrylonitrile are added, however, the polymer is "killed" since the polymerization of these monomers is self-terminating. This termination reaction which apparently involves the reaction of a carbanion end group with the ester group of the methacrylate, has been successful in the formation of graft copolymers. Thus Rempp and co-workers (217–219) added poly(methyl methacrylate) in tetrahydrofuran to poly(styrene) anions formed by polymerization of styrene with benzylsodium or phenylisopropylpotassium as catalysts. The poly(styrene) monocarbanion reacted with the ester groups to yield a graft copolymer in which poly(methyl methacrylate) formed the main chain and poly(styrene) the branches. Yields of grafting up to 40% were reported.

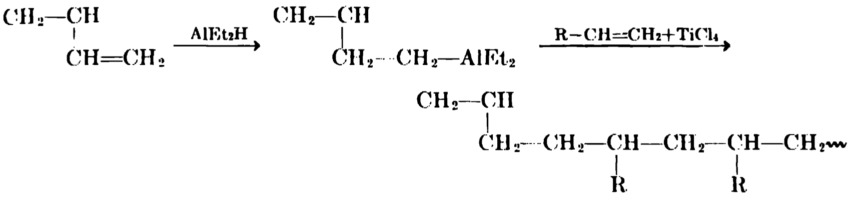
Poly(vinyl-2-fluorene) has been shown to form a metal complex with alkali metals in anhydrous tetrahydrofuran. The metallized polymers thus obtained, especially those containing lithium, were capable of anionically initiating the graft copolymerization of vinyl monomers. A poly(vinyl-2-fluorene)–poly(methyl methacrylate) graft copolymer was prepared by this technique (220). Poly(*p*-lithiostyrene) in the presence of butyllithium has also been found to initiate anionic graft copolymerization (221).

Gole, Goutière, and Rempp (222) prepared polyradical anions by reaction of polyvinyl aromatic compounds with alkali metals in tetrahydrofuran solution. These polyradical anions were capable of initiating the homopolymerization of vinyl monomers by electron transfer in a way similar to that of monoradical anions. The polymerization of ethylene oxide initiated by these anions, however, led to bond formation between the initiator and the polymer and graft copolymers were formed.

Dondos (223–225) has studied the preparation and use of poly(3,3-diphenyl-1-propene) in graft copolymerization reactions. Action of sodium naphthalene in tetrahydrofuran led to "metallation" of the carbon atoms adjacent to the two phenyl groups to a level of about 80%. These metallated centers acted as initiators on which methyl methacrylate and styrene graft copolymerized. Both multiple grafting, achieved by remetallation after the first grafting, and sequence grafting obtained by adding a new monomer to the "living" polymers already grafted, are reported.

Greber and Egle (226,227) prepared macromolecular organoaluminum compounds by reacting diethylaluminum hydride with polymers containing carbon–carbon double bonds. The polymeric aluminum alkyls upon reaction with transition metal halides, e.g., $TiCl_3$ formed active Ziegler–Natta-type catalysts which permitted graft copolymerization with α-olefins, as in Scheme 5.

Using a copolymer of styrene and butadiene as the backbone, the authors graft copolymerized ethylene, propylene, and styrene. In the case of propylene the graft copolymer had isotactic side chains (227). Similarly, by treating lithium alkyls or Grignard reagents with copolymers containing nitrile groups, macromolecules with nitrile–metal bonds were formed.



Scheme 5

These permitted grafting of acrylonitrile, methyl methacrylate, and 2- and 4-vinylpyridine. Macromolecules with C=O, C≡N, or C=C bonds, such as copolymers of styrene with vinylbenzophenone, acrylonitrile, or allylstyrene were also treated with alkali metals forming colored addition products. These polymer anion radicals, which resulted from electron transfer from the metal to the double or triple bond, initiated the anionic graft polymerization of acrylonitrile, methyl methacrylate, 2- and 4-vinylpyridine, butadiene, and styrene to form soluble graft copolymers.

Soluble organometallic macromolecules were also formed by the introduction of an alkali metal into halogen-containing polymer molecules (228,229). Thus the chlorine in poly(*p*-chlorostyrene) was exchanged for sodium by reaction of sodium naphthalene in tetrahydrofuran and the complex used to initiate the grafting of anionically polymerizable monomers. The grafted branches remained "live" and permitted further polymerization of added monomers to form a block-graft network.

The possiblity of initiating graft copolymerization with metal ketyls was demonstrated by Inoue (230,231), Zilkha (233), and others (232). Following along the same lines, Greber and Egle (234) prepared polymeric ketyls by reacting sodium with poly(vinylbenzophenone) at room temperature. Using this complex, grafting was initiated with acrylonitrile, methyl methacrylate, and 4-vinylpyridine. The authors also found that by reacting the ketyl in dioxane with further sodium the disodium derivative could be formed which, in addition to the above monomers, also polymerized styrene and allowed the preparation of graft copolymers with "living" side chains. Copolymers of styrene with methyl methacrylate, acrylonitrile, and alkenylstyrenes upon treatment with metallic sodium were also found to initiate graft copolymerization with anionically polymerizable monomers (235).

By reacting dimethylsilylmethylmagnesium chloride (Me_2SiHCH_2MgCl) with styrene acrylonitrile copolymers, macromolecular polymerization initiators were obtained which enabled the low-temperature graft copolymerization of 4-vinylpyridine, acrylonitrile, and methyl methacrylate.

The grafted branches were attached to the backbone by azomethine linkages and could be split off in the case of the 4-vinylpyridine graft by acid hydrolysis and isolated separately from the backbone polymer (236).

Greber and Egle (237) have also described the preparation of organotin and organolead substituted styrenes, their copolymerization with styrene, and the subsequent graft polymerization of ethylene using titanium tetrachloride as catalyst. By selective extraction with carbon disulfide the original copolymers were removed unchanged, and the graft copolymers characterized by their IR spectra.

Graft polymers of acrylonitrile, methacrylonitrile, and methyl methacrylate on polyhydroxy polymers such as cellulose, and poly(vinyl alcohol) have been prepared by anionic graft polymerization in liquid ammonia and other inert solvents at low temperature (238). The alkali alkoxide derivative of the polyhydroxy polymer backbone was used as the polymerization initiator.

Metal complexes of macromolecular polyfunctional Schiff's bases (239) and macromolecules with functional silicon organic groups (240) have been reported recently as anionic initiators of graft copolymerization. Shiota (303) made poly[(acrylonitrile-*co*-diketone)-*g*-propiolactone] with anionic catalyst such as KOH, CH_3 –ONa, or Bu – Li and studied the kinetics of solution polymerization in DMF and in bulk. Goutière (304,305) grafted poly(α-vinylnaphthalene) by anionic catalysis with ethylene oxide. Further studies were carried out on the grafting of poly(2-vinyl furan), poly(2-vinylfluorene) and copolymers with styrene.

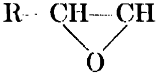
Ho (309) studied the grafting reactions and kinetics of chloromethylated polystyrene with methyl methacrylate catalyzed with butyl lithium. Baranov (307) prepared poly[(styrene-*co*-*N*-methacryloyl caprolactam(-*g*-ϵ-caprolactam] with a similar system, with sodium caprolactam as catalyst; Korshak (308) published the kinetics subsequently.

6. CONDENSATION AND RING OPENING REACTIONS*

Polymer molecules containing hydroxyl, carboxyl, amine, thiol, and certain ester groupings may be chemically linked together to form block and graft copolymers by a condensation reaction. Block copolymers are formed when these functional groups are at terminal positions while graft copolymers result if the functional groups on one of the polymers are at random positions along the chain. If both species contain the functional

*References for this subsection will be found on pages 45–54.

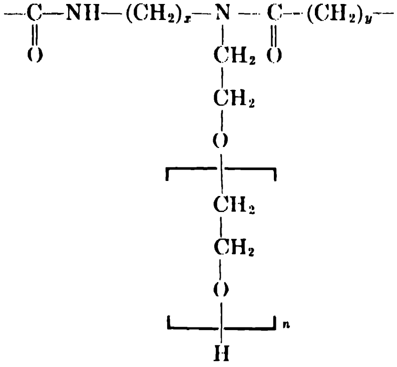
groups at random positions condensation linkages give a complex cross-linked structure.

Substances containing an active hydrogen atom can readily polymerize α-epoxides  $R-\underset{\diagdown\,O\,\diagup}{CH-CH}$ by a ring opening reaction. This reaction has led to the synthesis of a variety of block and graft copolymers by reacting such epoxides with macromolecules containing hydroxyl, carboxyl, or amide groupings. Indeed the first commercially successful block copolymers to be marketed were the nonionic detergents known as the Pluronics and Tetronics formed by the polyaddition of ethylene oxide with a poly(propylene oxide) thermal OH group (241). Ethylene diamine was also used to initiate the ring opening of the propylene oxide molecule and the tetrabranched poly(propylene oxide) so formed was used to initiate the block copolymerization of ethylene oxide. Another nonionic surfactant has been obtained by the combination of tetramethyldecynediol with two chains of ethylene oxide (242).

An interesting surface active graft copolymer has been reported by Mark (243). By copolymerizing styrene with 1–2 mole % vinyl acetate followed by hydrolysis of the acetate groups, a copolymer with widely spaced hydroxyl groups was obtained. These hydroxyl groups initiated the ring opening and graft polymerization of ethylene oxide to form a macromolecule containing both oil- and water-soluble segments. Similar water-dispersible graft copolymers have been reported by Weiss and co-workers (244). Copolymers of styrene and dimethyl maleate were converted to the copolymeric ethanolamide by reaction with sodium catalyzed monomethanolamine at its boiling point and the available hydroxyl groups used to initiate the polyaddition of ethylene oxide. Copolymers of styrene and allyl acetate were also prepared, the acetate groups saponified, and ethylene oxide grafted to the available hydroxyl groups in the backbone copolymer.

Attempts to graft cellulose (245) and poly(vinyl alcohol) (246) with ethylene oxide via the macromolecular OH groups yielded short polyethylene oxide chains due to the high reactivity of the secondary polymeric hydroxy groups. A high proportion of these chains consisted of only one oxyethylene unit and thus these polymers cannot be truly classified as graft copolymers. The Rayonier Company market an ethylene oxide modified wood cellulose material called Ethylose (247) for use in coated papers and in the textile and ceramic industry. The product is said to contain one ethylene oxide unit for each 20 cellulose units in the chain.

Interesting new derivatives of nylon with unusual properties have been prepared by treating nylon with ethylene oxide (248). These graft copolymers have greatly enhanced flexibility but still retain the high melting character of the original nylon. A hydroxyethyl 6-6 nylon containing 50% combined ethylene oxide was found to be flexible and useful over a very large temperature range, the polymer having a melting point of 221°C and an apparent second-order transition below −40°C. Analyses carried out to study the distribution of combined ethylene oxide residues in these materials indicated a tendency toward limited substitution of the nylon backbone and rather long average poly(ethylene glycol) branch lengths (see Scheme 6). This was attributed to the fact that the reactivity of the generated primary hydroxyl group is greater than that of the amide hydrogen



Scheme 6

toward ethylene oxide. Rafikov and co-workers (249) have achieved relatively high degrees (up to 55%) of grafting of ethylene oxide to films and fibers of polyamides which are not highly oriented. Crosslinking was found to occur as a result of the reaction of the terminal carboxyl groups of the poly(amides) and the hydroxyl groups of the poly(ethylene oxide) graft. Poly(acrylamide) films were also treated with ethylene oxide to form graft copolymers with up to 65% poly(ethylene oxide). The reaction was also accompanied by the formation of crosslinks.

Polyamide side chains have been grafted onto polymeric backbones by the reaction of appropriate functional groups with ε-caprolactam. Graft copolymers have been prepared from the lactam and styrene–butadiene rubber containing 1% methacrylic acid by heating the two components under pressure at 200–220° for 30 minutes (250). Styrene copolymers with acrylic acid, methyl acrylate, and maleic anhydride have also been reacted with caprolactam to yield grafts (251). Wichterle and Gregor (252) prepared copolymers of *N*-methacryloyl caprolactam with styrene and reacted them with caprolactam in the presence of alkaline catalysts. The monomer entered at the sites of the imide groups to form crosslinked graft polymers. The crosslinking was attributed to a Claisen condensation-type reaction between two diacyl imide groups.

Melville and co-workers (253) prepared a range of branched polymers by condensing poly(vinyl acetate) chains containing a terminal carboxyl group onto a radioactive, partially hydrolyzed backbone of poly(vinyl acetate). The important advantage of this process over normal grafting techniques is that the branches may be fractionated and characterized prior to attachment to the main chain. The average number of branches per molecule from the radiochemical analysis was found to vary between 5.5 and 40.

Kolesnikov and Tseng (254) have shown that mutual transesterification between carbochain polyesters and heterochain polyesters can lead to the formation of graft copolymers. This was demonstrated by heating mixtures of methyl methacrylate and ω-hydroxycarboxylic acids in the presence of a catalyst wherein grafting occurred by simultaneous polymerization, polycondensation, and mutual transesterification reactions. The authors have also reported graft copolymers formed by reaction of poly(methyl methacrylate) with poly(ethylene azelate) (255) and poly(hydroxyenanthate) (256), the reaction of acrylonitrile (257), styrene, and vinyl acetate (258) with the methacrylate of the polyester of ω-hydroxyenanthic acid and styrene–maleic anhydride copolymers with poly(hydroxyundecanoate) and poly(hydroxyenanthoate) (259).

By using a direct reaction between the acid chloride groups in a 1,1-dihydroperfluorooctyl acrylate–methacryloyl chloride copolymer and the hydroxy and amino groups present in the wool molecule, Pittman (260) was able to synthesize graft copolymers with improved properties. The treated wool samples were oil- and water-repellent, resistant to felting shrinkage, and resistant to acid, alkali, and oxidizing media. The hand and flexural rigidity were altered slightly, whereas wrinkle recovery, fabric break, tear strength, and abrasion resistance were not significantly changed. Besides rendering the polymer insoluble to dry-cleaning solvents, grafting permitted the use of smaller amounts of resin for shrinkage protection than was required with nongrafted polymer.

Polycondensation of polymers by the interfacial technique (261,262) is another technique which has been employed in the synthesis of graft copolymers. If two immiscible solvents, each containing a very reactive difunctional intermediate, are brought into contact, polycondensation can occur at the interface between the two solvents. Similarly, if the two immiscible solutions are brought into contact indirectly by first applying one solution to a substrate to provide an extremely thin layer of the solution on the surface and subsequently dipping the substrate into the second solution, an ultrathin film of the polymer is formed on the surface of the substrate. If the substrate contains reactive groups similar to those of the reactive intermediates, graft polymer formation ensues, the film is chemically anchored to the substrate.

When applicable, interfacial polycondensation offers many attractive features for the synthesis of graft copolymers (263). The reaction occurs almost instantaneously at room temperature; purity of reagents is less critical than in melt polymerization; the ratio of reagents is not critical; the reaction can be carried out in the presence of air under ordinary atmospheric conditions; and it can be employed with heat-sensitive substrates or heat-sensitive intermediates. The results obtained are influenced, however, by several reaction variables. These include the nature of the polymer, time of exposure of the substrate to the treating solutions, type of organic solvent used, concentrations of the treating solutions, the ratio of reagents used, and others (264).

Grafting by the interfacial condensation technique is particularly suited to wool systems. Wool contains $-$OH and $-$NH$_2$ groups which are present throughout the cross section of the fiber, including the surface; it is also readily wetted by either an aqueous solution (containing wetting agent) or by organic solvents. A detailed investigation into the synthesis of surface grafts on wool by interfacial polymerization has been carried out by Whitfield and co-workers (263). These authors present data which indicates that the grafting sites on wool are the free amino and hydroxyl groups located in the *N*-terminal amino acids or internal amino acids containing these groups in their side chain. Whitfield has reported the interfacial graft condensation of polyamides (264,265), polyurethans (266), polyureas, polyesters, polycarbonates (267), and a variety of copolymers onto the surface of wool.

Korshak, Vinogradova, and Lebedeva (268) have prepared graft copolymers from phenol–formaldehyde resin, isophthaloyl chloride, and 2,2-bis(4-hydroxyphenyl)propane by the interfacial polycondensation method.

Another interesting example of this method was recently described by Volgina (286). Telomers of acrylic acid were prepared with reactive halide terminals, which were subsequently reacted with β-aminoethyl cellulose to yield graft copolymers with well-identified side chains.

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7. RADIATION-INDUCED SYNTHESIS*

When electromagnetic radiation passes through matter its intensity decreases, primarily as a result of scattering and energy absorption by some of the irradiated molecules. Three major processes are operative.

1. The photoelectric effect.
2. Compton scattering.
3. The production of electron pairs.

For gamma rays from Co^{60} the predominant effect in organic materials is Compton scattering. In the Compton effect the incident gamma ray interacts with an orbital electron ejecting the electron from its orbit and producing another photon of lower energy. Both the electron and photon subsequently interact with the material or the surroundings giving rise to essentially two processes, one of ionization and the other of excitation. In the case of ionization the Compton electron transfers sufficient energy to the orbital electron of another atom to overcome the forces binding it to the nucleus. The electron is therefore ejected, leaving behind a positive ion. If the energy transferred is insufficient to cause ejection of an electron, the energy level of the atom is raised and the atom is said to be in an excited state. The ions and excited molecules are very reactive; they either react with other materials present in the system or decompose into radicals and atoms or molecules. The free radicals produced upon irradiation of polymeric systems may be used to initiate graft polymerization.

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* References for this subsection will be found on pages 103–116.

Grafting by means of radiation is by far the most popular synthetic technique and the majority of the literature on graft copolymerization published recently describes the use of a radiation method in one form or another. This fact is also reflected in the patent literature (see Part II of this volume) where the majority of the more recent applications claim a radiation-induced synthesis.

The growth in popularity of radiation as an initiating system stems from the improvement in availability and cost of the ionizing radiation as a result of the introduction over recent years of more powerful nuclear reactors. Apart from its cheapness, radiation is a very convenient method for graft initiation as it allows a considerable degree of control to be exercised over structural factors, such as the number and length of the grafted chains by careful selection of the dose and dose-rate. Radiation is also unique in its ability to enable grafting to be carried out on "prefabricated" or "shaped" articles.

The following sections review in a general sense the various methods of radiation grafting, their efficiency and applicability, and the kinetics and mechanism of the grafting reaction. There is also included an index (together with the appropriate references) of graft copolymers prepared by a radiation synthesis which has been compiled from the literature available to date.

A. The Different Methods of Radiation Grafting

As has been indicated above the irradiation of organic macromolecules leads predominantly to the formation of free radicals. If the irradiation is carried out in air, an effective free radical scavenger, peroxides and hydroperoxides are formed within the polymer. If, however, the polymeric substrate is highly crystalline and in particular if the irradiation is carried out at low temperature and in the complete absence of air, the free radicals can be trapped in the system and can remain "active" for a considerable time. The free radicals, peroxides, and hydroperoxides formed or trapped in polymeric substrates upon irradiation can be used quite conveniently to initiate block and graft copolymerization. Experimentally then, radiation synthesis of graft and block copolymers can be accomplished by the following methods.

1. The direct or mutual irradiation of a polymer in the presence of a monomer and in the absence of air.

2. The preirradiation of a polymer in air to yield peroxy groups and the subsequent contact with a monomer in the absence of air.

3. The preirradiation of a polymer *in vacuo* to yield trapped radicals followed by heating in the presence of another monomer, in the absence of air.

4. The irradiation of two polymeric substrates in intimate contact and in the absence of air.

5. The irradiation in air of polymer latices swollen with monomer.

Apart from discussing the more important aspects of each method, no attempt will be made to review in detail the individual work of the numerous authors in these fields. For more detailed studies, especially of grafting to poly(ethylene) and poly(propylene) systems, the reader is referred to Chapter XII of Chapiro's book *Radiation Chemistry of Polymeric Systems* (41). A list of graft copolymers that have been prepared by the above methods has, however, been compiled and is included in Table II (p. 74). The polymers are arranged in alphabetical order and are grouped according to the method of preparation. A brief description of the work reported in the reference is also included. This table has been compiled from the general literature available to May, 1966.

In Part II, Appendix VI, of this volume, the radiation-induced techniques of graft copolymerization are also listed together with a comparison of the first mention of the method in both the general and patent literature.

1. The Direct Grafting Method

In its simplest form the direct grafting method involves the irradiation of a polymeric substrate in the presence of a monomer and in the absence of oxygen. Graft copolymerization of the monomer to the polymer is then initiated through the free radicals generated in the latter.

A number of important factors must be considered, however, before applying the direct radiation method to a given polymer–monomer system. Ionizing radiation as such is unselective. One must therefore consider not only the effect of radiation on the polymeric substrate but also the effect on the monomer, the solvent, or any other substance present in the system.

The radiation sensitivity of a substrate is measured in terms of its G_r value or free radical yield which is the number of free radicals formed per 100 eV energy absorbed per gram. The highest grafting yields will occur for polymer–monomer combinations in which the free radical yield of the polymer is much greater than for the monomer. It also follows that the grafting yield will increase the lower the monomer concentration. The free radical yield of a monomer can be directly derived from the kinetics of its radiation polymerization and from experiments with free radical scavengers. For polymers the situation is a little more complex and G_r values have to be estimated from data on low molecular weight analogs. Table I, which has been extracted from Chapiro's book (41), lists G_r values for some polymeric and monomeric substrates.

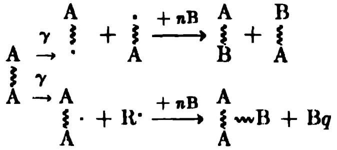
TABLE I

Approximate G_r Values of Monomers and Polymers

Monomers	G_r	Polymers	G_r
Butadiene	Very low	Poly(butadiene)	2.0–4.0
		Poly(isoprene)	
Styrene	0.69	Poly(styrene)	1.5–3.0
Ethylene	4.0	Poly(ethylene)	6.0–8.0
		Poly(isobutylene)	
Acrylonitrile	5.0– 5.6	Poly(methyl methacrylate)	6.0 or 12.0
		Poly(vinyl acetate)	
Methyl methacrylate	5.5–11.5	Poly(methyl acrylate)	
Methyl acrylate	6.3	Silicones	3.6 or 7.2
		Cellulose	10.0
Vinyl acetate	9.6–12.0	Poly(vinyl alcohol)	
		Poly(vinyl chloride)	10.0–15.0
Vinyl chloride	10.0	Poly(vinylidene chloride)	

The use of this type of representation in choosing likely polymer–monomer combinations for use in the direct radiation technique should, however, be treated with caution. It has been observed, for example, that the G_r value of an irradiated system is sometimes markedly altered by the presence of another species. Turner (284) found that whereas the free radical yield for rubber obtained as a result of crosslinking experiments was of the order of 3, in the presence of styrene this figure dropped to 0.26. This phenomenon, known as the "protective effect," has been attributed to an energy transfer between the different species present. A similar effect was noticed by Sebban-Danon (232) in the styrene–poly(isobutylene) system.

Together with the radiation sensitivity of the polymer–monomer combination one must also consider the effect of the radiation on the actual polymeric substrate. In general, polymers either degrade or crosslink under irradiation. If the polymer degrades then irradiation in the presence of a monomer will lead predominantly to block-type copolymers; if the polymer crosslinks, graft structures will result. This may be represented schematically as in Scheme 7 (41):



(1)

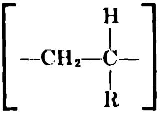
(2)

Scheme 7

(Note the formation of homopolymer which occurs in case 2.)

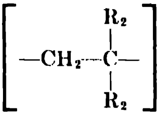
Here $A\sim\cdot$ and $A\dot{\sim}A$ represent polymeric free radicals derived from Ap and $R^{\cdot}$ represents a low molecular weight radical or hydrogen atom.

As a general empirical rule it may be stated that when the structure of a vinyl polymer is such that each carbon atom of the main chain carries at least one hydrogen atom, the polymer crosslinks (case I), whereas if a



$$\left[-CH_2-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-\right]$$

(I)



$$\left[-CH_2-\overset{\displaystyle R_2}{\underset{\displaystyle R_2}{C}}-\right]$$

(II)

tetrasubstituted carbon atom is present in the monomer unit, the polymer degrades (case II) (41).

The dose and dose-rate of irradiation are important factors in any radiation grafting system. In the direct method the total dose determines the number of grafting sites while the dose-rate determines the length of the grafted branches. The length of the branches is also controlled by other factors, such as the presence of chain transfer, the concentration of monomers, the reaction temperature, the viscosity of the reacting medium, diffusion phenomenon, etc.

Diffusion of the monomer into the polymer plays an important role in the direct radiation method as it is by this means that the monomer reaches the active sites within the polymer. It would be expected that the rate of graft polymerization would be directly proportional to the radiation dose-rate. In some cases, however, the diffusion of monomer cannot satisfy the increased rate of initiation within the polymer. Chapiro and co-workers (48,54), for example, found that for the system styrene–poly(tetrafluoroethylene) homogeneous grafting of the styrene occurred up to a certain dose-rate value but above this dose-rate only surface grafting was encountered. The monomer diffusion could not keep up with the rate of initiation with the polymer.

In some direct radiation grafting systems an autocatalytic effect has been observed (25,48,52,54; from 318). This accelerated rate is probably due to the gel effect which results from a slowing down of the termination step due to lack of mobility of the growing chains. Hoffman and co-workers (102) studied the irradiation grafting of styrene to high- and low-density polyethylene film and noticed in some cases that grafting continued after irradiation had ceased. This again is probably due to the presence of occluded chains which are unterminated.

The presence of solvents and additives such as chain transfer agents can have a marked effect on the grafting yield. Restaino and Reed (191) studied the graft copolymerization of vinyl acetate to films of poly(tetrafluoroethylene) by the direct radiation method. They found that the addition of small quantities of CCl_4 resulted in a decrease in the rate of grafting as well as a decrease in the molecular weight of the homopolymer formed. The decrease in grafting rate was attributed to a smaller G_r value for radical formation of CCl_4 when compared to that for vinyl acetate and to the differential rate of chain transfer between CCl_4 and grafted poly(vinyl acetate) with the vinyl acetate radical.

Sakurada and co-workers (226) found a similar effect when divinylbenzene was added during irradiation of a styrene–nylon 6 system. These authors also noted a marked acceleration in the grafting rate with the addition of small amounts of polar substances such as 1% water or 3% methyl alcohol. This effect has been noticed quite often and occurs with both polar (56,67,226,263,297) and nonpolar polymers (71,169). These solvents probably increase monomer–polymer contact in the case of polar polymers and enhance the gel effect in the case of nonpolar polymers. They may also increase the rate of initiation due to energy transfer or due to reactions of the solvent radicals with the polymer or monomer (318).

The effect of temperature on the kinetics of the direct radiation method is quite complex. Increase in temperature increases the monomer diffusion rate but also increases transfer and termination reaction rates of the growing chains, reducing the importance of the gel effect. Solubilities and radical mobilities may also change as the temperature is varied (318).

It will be appreciated that in the direct radiation method a certain amount of homopolymer will always be formed both because of the effect of the radiation on the monomer and as a normal consequence of the grafting reaction (see eq. 2). Contamination of the grafted product with homopolymer can be quite inconvenient as by and large most polymers are incompatible and due to a segregative tendency, the presence of physically mixed polymer impurity can yield a product with poor physical, optical, and electrical properties. The direct radiation method is, on the other hand, by far the most efficient technique since it involves rapid utilization of the accessible backbone polymer radicals as they are formed. It is not surprising then that numerous techniques have been developed in an effort to reduce the amount of homopolymerization formed during the reaction. This is particularly evident in a study of the patent literature on radiation grafting (see Part II, Appendix VI, of this volume).

To avoid homopolymer formation the chief problem is to ensure true molecular contact between monomer and polymer. Even if this is initially established, it needs to be maintained during the radiation treatment while the monomer is undergoing conversion. Charlesby and Pinner (38) and, later, other workers (48,71,96) attempted to overcome this problem by using an "intermittent" technique in which the monomer was allowed to diffuse freely through the polymer between bursts of irradiation. Zimmerman (316,317) suggests that homopolymer formation could be reduced considerably by maintaining during the irradiation a temperature sufficiently low so that the monomer to be grafted cannot polymerize.

Armstrong and Rutherford (13–16) developed a method of grafting vinyl monomers onto fiber substrates by the direct radiation method which resulted in less homopolymer formation and more homogeneous products. The fibrous materials were irradiated in the presence of monomer *vapor*. An increased rate of grafting was also noted when small amounts of water, methanol, or acetic acid vapors were present.

2. Preirradiation in Air

In this method the polymeric substrate is irradiated in air or oxygen to produce peroxide bonds. These peroxide groups are reasonably stable and the polymer can be stored in the cold without loss of activity. If heated subsequently in the presence of monomer (as liquid or vapor) to about 150° in the absence of air, the peroxide groups decompose liberating free radicals which can then initiate graft polymerization. This method has been developed extensively by Chapiro (46,47,50).

In principle the preirradiation method should not yield homopolymer because the monomer is never directly exposed to radiation. In some cases, however, there is evidence that irradiation in air leads to the formation of hydroperoxides on the polymer backbone. These, on heating, decompose giving a hydroxyl radical which can initiate the homopolymerization of the added monomer. Poly(propylene) in particular appears to form a considerable amount of hydroperoxide groupings on irradiation in air (50). Homopolymer formation can, however, be reduced considerably by the incorporation of a redox system during irradiation to convert the hydroxyl radicals to hydroxyl ions. Hachihama and Takamuka (85) added ferrous ion to the irradiated polymer while Minnema et al. (151) found that a ferrous acetylacetone–ferric acetylacetone system in the presence of benzoin was quite effective in reducing homopolymerization initiated through decomposition of hydroperoxide groups. Homopolymer can further arise during the grafting process by the dissociation of low molecular weight peroxides ROOR, ROOH, H_2O_2 which may be present in the irradiated polymer. Smith, McMillan Mann, and Salman in a British Patent to B.X. Plastics (Part II of this volume; 279) claim that extraction of the irradiated polymer with an appropriate solvent prior to the grafting operation can be quite effective in removing these low molecular weight peroxides.

The efficiency of the grafting reaction will depend directly on the kinetics of the radiation peroxidation process. The peroxide yield will necessarily depend on both the G_r value of the irradiated substance and the stability of the resulting peroxide at the irradiation temperature; however, detailed studies on the mechanism of polymer peroxide formation is scarce. In his *Radiation Chemistry of Polymeric Systems* (41), Chapiro suggests that the peroxidation process occurs through radical–radical combinations involving peroxidic radicals:

$$\text{Ap} \xrightarrow{\gamma} 2\text{P}\cdot \ (\text{or } \text{P}\cdot + \text{R}\cdot) \tag{3}$$

$$\text{P}\cdot + \text{O}_2 \rightarrow \text{PO}_2\cdot \tag{4}$$

$$\text{PO}_2\cdot + \text{P}\cdot \rightarrow \text{PO}_2\text{P} \tag{5}$$

$$\text{PO}_2\cdot + \text{PO}_2\cdot \rightarrow \text{PO}_2\text{P} + \text{P}_2 \tag{6}$$

For polymers containing labile hydrogen atoms (such as poly(propylene)) chain peroxidation can lead to hydroperoxide formation (PO_2H).

If it is assumed that the peroxidation occurs only by the processes outlined in eqs. 3–6, then one would not expect that the dose-rate of preirradiation would seriously affect the peroxide yield. Dose-rate does, however, become important when the rate of diffusion of oxygen within the polymer is such that it cannot keep up with the polymer radical formation. When this situation arises, crosslinking and degradative reactions in the polymer predominate but, in general, the problem may be overcome by increasing the oxygen pressure during irradiation. The concentration of polymer peroxides will increase with radiation dose. For low doses the peroxide concentration has been shown to build up linearly until for very high doses radiolysis of the peroxide groupings becomes significant and a reduction in the apparent overall rate of peroxidation is noticed (41). The peroxide concentration in the backbone polymer determines the number of grafting sites while the length of the branches can be controlled by appropriate selection of the grafting temperature and monomer concentration.

It has been reported that the presence of solvents during the preirradiation step can increase the yield of active sites and hence the ultimate grafting yield. Kobayashi (123), for example, studied the grafting of styrene to cellulose and found that the reaction proceeded to a higher grafting level in hydrogen peroxide than in either air or water. The increased grafting yield was quite markedly dependent on the hydrogen peroxide concentration. Durup (77) notices a similar effect with chloroform.

Although perhaps a little less efficient than the direct grafting method the preirradiation technique has the important advantage of the avoidance of direct radiation polymerization of the monomer. The irradiation of polymer in air is also a very simple and convenient operation although the subsequent heating to 150° that is needed to liberate the free radicals requires a thermally stable polymer.

3. Grafting Initiated by Trapped Radicals

One of the primary effects of ionizing radiation on polymers is the formation of free radicals. Although free radicals are highly reactive it has been demonstrated that they can become trapped for extremely long periods (several days or even months) in a viscous medium such as that encountered in a polymer at a temperature below its glass transition point. If the polymer is partly crystalline, the free radicals formed within the crystalline regions upon irradiation are still more firmly trapped, since the mobility of polymeric segments is much lower if these are involved in an organized structure. Although the free radicals are trapped they are still highly reactive and provided the monomer can diffuse through the polymer to reach the reactive sites, the trapped radicals can be used to initiate graft copolymerization (27,32,43,304). If oxygen or air is present during the irradiation, peroxide formation occurs as has been discussed in the previous section.

The grafting yield obtained by this method will depend directly on the efficiency of radical trapping. Radical mobility is a function of temperature and the physical state of the system; it follows therefore that the most efficient radical trapping will occur for crystalline polymers irradiated at low temperature. The concentration of free radicals in an irradiated polymer has been shown to increase linearly with dose but tends to reach a limiting value for a certain dose. This limiting dose is apparently a function of the particular polymer system and has to be determined experimentally (41). The use of electron spin resonance spectrometry has made the study of the formation and decay of free radicals quite convenient as the technique is particularly suited to polymeric systems (319,246,117).

As with the peroxidation technique, homopolymer formation should not occur in this process as the monomer is not exposed to radiation. Moreover, low molecular weight radicals, which would also initiate homopolymerization, are not expected to remain trapped at ordinary temperatures. Kesting and Stannett (117), however, report homopolymer formation in a study of the grafting of styrene to cotton–cellulose that had been vacuum irradiated in the presence of small amounts of water. The viscosity average molecular weight of the grafted product was found to vary by only about 20% across a fortyfold variation in total dose. Kesting and Stannett suggest that this low dependence of molecular weight on the total dose is probably due to a considerable amount of chain transfer, which would also explain the large proportion of homopolymer formed.

Shinohara and Tomisha (246) studied the grafting of styrene, acrylonitrile, and *N*-vinylpyrrolidone to high density poly(ethylene) preirradiated in both air and vacuum and found that even in the air-irradiated polymer, radicals were present which could induce graft copolymerization. This result was contrary to earlier work by Chapiro but the authors indicate that this may be due to differing irradiation conditions. Chapiro's work involved low dose-rates and long irradiation time such that any free radicals produced would have disappeared almost completely during irradiation. Shinohara also examined the effect of storage of the irradiated polymers in air at various temperatures and found that the grafting activity decreased gradually with storage time; the higher the temperature, the faster the decreasing rate. For high-density poly(ethylene) irradiated to 10 Mrad at room temperature, the free radical content as determined by electron spin resonance spectrometry was reduced by one-half after 50 hr storage at 20°C.

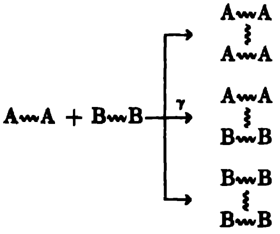
When the irradiated polymer was stored in vacuum (10^{-2} mm Hg) radical decay still occurred although to a much lesser extent than in air. This decrease of radical content is probably due to mutual recombination of radicals and/or reaction with survived and trapped oxygen in the system.

The efficiency of the trapped radical method of grafting is not as good as for the peroxidation method because of the very low concentration of frozen-in radicals that can be achieved. The limited lifetime of these radicals also means that the grafting reaction must be carried out almost immediately after the irradiation. Perhaps the only advantage of this method over the peroxidation technique is the fact that the temperature required for the grafting reaction to occur is much lower. This makes the method useful for polymers with a poor heat stability.

In both of the preirradiation techniques discussed above the total dose required for a given degree of grafting is of the order of megarads while only tenths of a megarad are required using the direct irradiation method. This fact becomes important when grafting to the more radiation-sensitive polymers is required.

4. *Irradiation of Polymer Mixtures*

If an intimate mixture of two or more polymers is irradiated, it is possible that a crosslinking type of reaction will occur with the formation of some graft copolymers. The efficiency of this process depends on obtaining close physical contact between the different components and, as most polymers are incompatible this technique, has found only limited use. The type of polymer present and the reactions they undergo under irradiation is another important factor. Thus if the mixture contains two polymers of the crosslinking type reactions 7–9 are expected to occur (41):

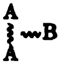


(7)

(8)

(9)

If one of the polymers, say B_q, is of the degrading type, one can still expect the formation of grafted structures such as



However, if both polymers are of the degrading type, the yield of graft (or block) copolymers is very small.

Little work has been reported in this field and the majority of graft copolymers prepared by this method appear in the patent literature (see

Part II, Appendix VI, of this volume). Even if we assume that the polymers are completely compatible and the intimate contact between the polymer chains has been achieved it can be seen from eqs. 7–9 that the grafting efficiency cannot be expected to exceed about 30% as each of these reactions has an equal probability of occurring. It is not surprising then that this method has received little attention in the general literature. In fact the only detailed investigation of this technique available to date is the work of Henglein (91) who irradiated mixtures of poly(vinylpyrrolidone) and poly(acrylamide) in aqueous solutions.

5. Radiation Grafting in Emulsion Systems

If the irradiation of a polymer–monomer combination is carried out in emulsion the reaction medium does not become unduly viscous at high conversions and the system remains homogeneous throughout the duration of the reaction. Homogeneous grafting in emulsion results in high grafting efficiencies with less homopolymer formation and it is therefore a very attractive method of grafting. The copolymerization can be initiated by free radical sites formed on the backbone as a result of several reactions: (*a*) direct action of the irradiation on the polymer, (*b*) removal of a hydrogen atom from the polymer by hydroxyl radicals produced by the irradiation of the aqueous phase, and to a lesser extent by chain transfer and the formation of buried polymer radicals.

It is not surprising that the majority of grafting work using this technique has been done on natural rubber latices. Several authors (10,59–64,89,90) have reported detailed studies on the grafting of methyl methacrylate and styrene to natural rubber latices using Co^{60} irradiation and in each case good grafting yields with little homopolymer formation were obtained, even at relatively high monomer concentrations. In order to explain the high yield of graft copolymer Cooper and Vaughan (62) proposed a reaction mechanism assuming a relatively slow initiation step between rubber radicals and methyl methacrylate and a rapid crossed termination reaction between methacrylate radicals and rubber radicals. The authors further assumed that radicals produced from methyl methacrylate by radiation are, unlike the growing methacrylate chains, capable of attacking the rubber molecules and thus form sites for grafting to occur. Monomer transfer was assumed to be negligible. Later work on the molecular weight determination of the methyl methacrylate–natural rubber graft by column fractionation (63) indicated a broad distribution with peaks of low and high molecular weight polymer. The distributions were insufficiently defined to make definite assignments to the speeds of the reactions involved but were not inconsistent with the mechanism proposed above.

Cockbain, Pendle, and Turner (59,60) also prepared graft copolymers from natural rubber latex and methyl methacrylate using γ-irradiation and compared the results with the same reaction initiated by a redox catalyst. Graft copolymers prepared by the redox catalyst are known as MG rubbers while polymers prepared in emulsion by irradiation are called MGI rubbers. An investigation of the colloidal and filmforming properties of the two polymer latices showed striking differences. For example, an MGI latex in which 28% by weight of the total polymer was poly(methyl methacrylate) formed a continuous coagulum on acidification, whereas the corresponding MG latex gave discrete floccules. The MGI latex also yielded a continuous coherent and highly elastic film on drying, whereas the MG latex gave a discontinuous, cracked film. Although the poly(methyl methacrylate) was of higher molecular weight in the MGI rubber and a lower proportion was present as free polymer, such differences could not account for the superior film-forming properties of the MGI latex. Further experimental work was carried out using water- and oil-soluble polymerization retarders, the results of which showed that the reason for the superior properties of the latex prepared using radiation was that the graft polymerization took place within the polymer particles since, if a retarder such as *tert*-dodecyl mercaptan, soluble in the oil phase was added, the films obtained were cracked. Similarly, a more uniform distribution of the polymer was obtained upon the addition of water-soluble retarders. It was concluded, therefore, that the distribution of polymerized monomer within the individual particles of the latex was the major factor in determining its film-forming characteristics and colloidal behavior. Cockbain and Pendle stress the importance of this principle, pointing out that it should be relevant to many emulsion copolymerization reactions in which the composition of the copolymer changes with percentage conversion of the monomer, particularly when the emulsion particles approach in size those of natural rubber latex.

Hayden and Roberts (89,90) extended the technique to systems other than natural rubber and studied the gamma ray-induced grafting of acrylonitrile to poly(vinyl acetate) and poly(methyl methacrylate), ethyl acrylate to poly(methyl acrylate), and methyl methacrylate to poly(ethyl acrylate), and vinyl acetate were also grafted to poly(tetrafluoroethylene) by subjecting a commercial Fluon latex, swollen with monomer to the action of gamma rays. Irradiations were carried out at various temperatures ranging from room temperature to 80°C and no attempt was made to exclude air from the system. The grafting efficiency was found to be quite temperature-dependent, little or no monomer entering into copolymerization at room temperature. The highest degrees of grafting were obtained with styrene at 80°C and with butyl methacrylate at 55°C, and these amounted to 8% grafted.

The emulsion technique appears most effective for the grafting of vinyl monomers to natural rubber systems, the reaction proceeding quite smoothly at room temperature with the minimum production of homopolymer. An added advantage is that complete exclusion of air from the system is not necessary. For film-casting work the radiation-initiated system is infinitely better than the conventional redox method, but for normal radiation grafting work the method has the disadvantage that it requires the polymer to be in the form of a stable emulsion. The work of Hayden and Roberts indicates that the reaction does not proceed as smoothly for nonrubber systems and even after irradiation of up to 4×10^5 rads, application of heat was necessary for any appreciable grafting to occur.

The discussion up to this point has tacitly assumed the use of Co^{60} γ-radiation as the graft copolymerization initiator. It should be pointed out, however, that other types of radiation are just as effective in initiating grafting and indeed have been used by many authors. In general, the grafting mechanism is the same for all types of radiation, be it α, β, γ, or x-rays as in each case the end result is the formation of free radicals. Odian and co-workers (166) carried out a comparison of radiation-induced graft copolymerization using electron accelerators and isotope sources as radiation initiators. They investigated the grafting of methacrylic acid–styrene mixtures onto poly(propylene) film. Similar results were obtained for the two initiating systems with the exception that the isotope-initiated grafts appeared to be slightly richer in the more polar component than the equivalent accelerator-initiated grafts.

The use of β-particles produced from a Van de Graaff accelerator has the advantage of supplying quite high dose-rates which would be difficult to obtain with a Co^{60} source. Dose-rates of the order of 2 Mrad/min can be quite conveniently obtained from a 2 MeV accelerator. High energy x-rays can be used to give dose-rates intermediate between those of linear accelerators and Co^{60} sources.

The Japanese workers Umezawa and Hirota (99–101,288–292,295) have used secondary α-rays produced by the ${}^{10}B(n,\alpha){}^{7}Li$ reaction to initiate grafting to poly(ethylene) and poly(propylene) film and fiber. α-Ray penetration is only of the order of 10^{-3} cm which enables "surface grafting" to be carried out quite successfully leaving the inner regions of the polymeric substrate free of radiation damage.

B. Kinetic Features of Radiation Grafting

Accurate kinetic data is necessary for the optimum design of graft polymerization processes as the rate of grafting and the location of the grafted branches within the polymeric substrate can affect the properties of the copolymer formed. In principle, the conventional free radical polymerization scheme should be applicable to radiation–grafting systems as, in general, the reaction involves the polymerization of a vinyl monomer initiated by a polymeric radical. In practice, however, the situation is not quite as straightforward as this because of the number of specific features that result from the special reaction conditions prevailing in most grafting systems. The gel effect, chain transfer, phase separation, and diffusion effects are but a few of the many factors which can seriously affect the reaction kinetics.

1. The Direct Radiation Technique

Consider the simplest case of polymer swollen by or immersed in a monomer, the polymer being completely insoluble in the monomer. If one assumes that the graft polymerization occurs by a radical chain process then the overall reaction scheme can be divided into three main steps: initiation, propagation, and termination. This may be represented as follows (from 165).

Initiation:

$$\mathrm{P} \xrightarrow{k} \mathrm{P}^{\cdot} \tag{1}$$

$$r = kI \tag{2}$$

Propagation of initial radical:

$$\mathrm{P}^{\cdot} + \mathrm{M} \xrightarrow{k_i} \mathrm{PM}^{\cdot} \tag{3}$$

$$r_i = k_i[\mathrm{P}^{\cdot}][\mathrm{M}] \tag{4}$$

Propagation:

$$\mathrm{PM}_n^{\cdot} + \mathrm{M} \xrightarrow{k_p} \mathrm{PM}_{n+1}^{\cdot} \tag{5}$$

$$r_p = k_p[\mathrm{PM}_n^{\cdot}][\mathrm{M}] \tag{6}$$

Termination by two growing radicals:

$$\mathrm{PM}_m^{\cdot} + \mathrm{PM}_n^{\cdot} \xrightarrow{k_t} \mathrm{PM}_{m+n} \quad \text{or} \quad \mathrm{PM}_m + \mathrm{PM}_n \tag{7}$$

$$r_t = 2k_t[\mathrm{PM}^{\cdot}]^2 \tag{8}$$

If one makes the normal assumption that the length of the polymer chains is long, then reaction 3 can be neglected with respect to reaction 5, and one obtains the following relation for the rate of graft polymerization:

$$r_p = k_p[\mathrm{PM}_n^{\cdot}][\mathrm{M}] \tag{9}$$

Introducing the conventional steady-state assumption that the rate of change of the radical concentration is small compared to its rates of formation and disappearance, then

$$k_i[\mathrm{P}^{\cdot}][\mathrm{M}] = 2k_t[\mathrm{PM}_n^{\cdot}]^2 \tag{10}$$

i.e.,

$$r_i = 2k_t[\mathrm{PM}_n^{\cdot}]^2 \tag{11}$$

$$\therefore \quad [\mathrm{PM}_n^{\cdot}] = (r_i/2k_t)^{1/2} \tag{12}$$

On combining eq. 9 and 12 one obtains for the rate of graft polymerization:

$$r_p = k_p[\mathrm{M}]\,(r_i/2k_t)^{1/2} \tag{13}$$

where

I = intensity of radiation
P = backbone polymer
$\mathrm{P}^{\cdot}$ = polymer radical
PM_m, PM_n, or PM_{m+n} = graft copolymer
M = grafting monomer
r = rate of initiation of polymer radicals
r_i = rate of initiation of graft reaction
r_p, r_t = rate of propagation and termination respectively
k = rate constant for initiation of polymer radicals
k_i = rate constant for initiation of graft reaction
k_p, k_t = propagation and termination rate constants, respectively

Equation 13 can be written in the form

$$r_p = K[\mathrm{M}] \tag{14}$$

where

$$K = k_p(r_i/2k_t)^{1/2} \tag{15}$$

It is perhaps not strictly correct to assume a steady state of free radicals capable of initiating the graft copolymerization. Restaino and Reed (191), however, have shown that for the grafting of vinyl acetate to poly(tetrafluoroethylene) film the steady-state assumption is quite justified. The authors point out, however, that this steady state applies to the radicals formed at the surface of the polymer film and not to the free radicals within the film, which in some cases are capable of very long lifetimes.

It has been further assumed in the above derivation that chain transfer reactions are negligible. This is not always a valid assumption for, whenever a monomer is polymerized in the presence of a polymer, chain transfer to the polymer or transfer to the monomer will always occur to some extent. Chain transfer may be represented by the following processes:

1. Transfer to monomer:

$$\mathrm{PM}_n^{\cdot} + \mathrm{M} \xrightarrow{k_{tr.m}} \mathrm{PM}_n + \mathrm{M}^{\cdot}$$

2. Transfer to polymer:

$$\mathrm{PM}_n + \mathrm{M}^{\cdot} \xrightarrow{k_{tr.p}} \mathrm{PM}_n^{\cdot} + \mathrm{M}_n$$

which in either case can lead to further homopolymer or graft polymer formation.

The rate of propagation of the initial polymeric radical depends directly on the intensity of the radiation. From eq. 13, then, it can be seen that the rate of graft copolymerization will be dependent on the square root of the radiation intensity. Experimental verification of this fact, however, has only been successful in cases where the grafting has occurred only at the polymer surface. Chapiro (48), for example, studied the influence of dose-rate on the grafting of styrene to poly(tetrafluoroethylene) and found that at low dose-rates the instantaneous grafting rate obeyed a square-root law to a good approximation but above a critical dose-rate the rate suddenly dropped. In this range of dose-rates the graft copolymer was limited to a surface process. Similar results were obtained by Restaino and Reed (191) for poly(tetrafluoroethylene-*g*-vinyl acetate) and by Ballantine et al. (25) for the poly(ethylene)—acrylonitrile system. The observations indicate that there is superimposed upon the normal graft polymerization reaction the simultaneous effect of monomer diffusion into the polymer.

The effect of monomer diffusion should manifest itself by yielding slower grafting rates to thick polymer films compared to thin films. Several investigators have studied the effect of sample thickness on the grafting of styrene to poly(ethylene) with apparently conflicting results. Thick poly(ethylene) films have been observed by Ballantine et al. (25,26,58) to have significantly higher rates of fractional weight gain at room temperature than thinner ones. Hoffman and co-workers (102) reported a similar effect at higher grafting temperatures (40°C); however, they observed the opposite trend at 10–20°C and no thickness effect at 70°C. Charlesby and Pinner (38) exposed styrene-swelled poly(ethylene) films to 2 Mev electrons at an absorbed dose of 3 Mrad/min; they found that the weight gain per megarad was the same whether the dose was administered continuously in a single exposure or intermittently with additional equilibration with styrene between electron bursts. At least some of these anomalous thickness effects can be accounted for if it is assumed that variations in crystallinity as well as additive content can be expected in films that differ, nominally, in thickness only. There is in fact good evidence that styrene dissolves and reacts primarily in the amorphous regions of poly(ethylene) so that samples of differing crystallinity would give rise to apparent inconsistencies in grafting rate (247).

To account for the effect of monomer diffusion Chandler et al. (39) applied Frick's law to the basic graft equation (eq. 13) and obtained the following expression for the concentration C of the diffusing monomer at any point x in the polymer at time t.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - KC \tag{16}$$

where D = diffusion coefficient and K = defined by eq. 15.

Using this expression Chandler derived an equation for Q, the amount of monomer grafted per unit volume, after time t:

$$Q = \frac{8KC_1t}{\pi^2}\sum_{n=1,3,5\ldots}^{\infty}\frac{1}{n^2}\left(\frac{a}{a+K}\right) - \frac{8KC_1}{\pi^2}\sum_{n=1,3,5\ldots}^{\infty}\frac{1}{n^2}\left\{\frac{K}{(a+K)^2}\right\}\{e^{-(a+k)t}-1\} \tag{17}$$

where C_1 = saturation concentration of monomer in the polymer and $a = \pi^2n^2D/l^2$, where l = thickness of the film.

Since the film thickness, l, the diffusion coefficient, D, and the solubility of the monomer in the polymer, C, are readily obtainable, determination of the amount grafted per unit volume, Q, as a function of time, t, permits evaluation of H. Further knowledge of the initiation rate r_i then permits evaluation of the ratio k^2_p/k_t.

Chandler (39) applied eq. 17 to the grafting of styrene to poly(ethylene) but found that the k^2_p/k_t value for the reaction was about a thousand times as large as that for homopolymerization of styrene at the same temperature. Chandler explained this result in terms of a decrease in the termination rate constant k_t due to an increase in the viscosity of the reacting medium during grafting (the gel effect). Silverman and co-workers (247) have pointed out, however, that the discrepancy in the result is more likely due to the fact that the majority of weight increase in grafted films is due to occluded homopolymer which cannot be removed even by prolonged extraction. Silverman carried out a microscopic examination of styrene-grafted poly(ethylene) films and found that the actual amount of grafted styrene was considerably less than the weight gain. Thus the rate constants derived by Chandler, and in fact by most authors who have carried out kinetic observations based on the weight increase of "extracted" films, do not apply to the actual grafting reaction.

In an attempt to overcome this problem of occluded homopolymer in grafted films, Silverman carried out grafting experiments on polyethylene fluff, the polymer being in the form of rodlike and spherical particles about 3–10 mμ in diameter. Silverman argues that the extra dimension available to the extracting fluid makes it easier for the solvent to remove the homopolymer. The results indicated that to a good approximation the grafting process could be described by the quasi homogeneous model with square root dependence upon gamma exposure rate as proposed by Chandler.

Mock and Vanderkooi (154) attempted to take account of the diffusion effect in an examination of the kinetics of the direct grafting of styrene to ethyl cellulose film. From a study of the rate of permeation of styrene vapor through an ethyl cellulose film while subjecting the film to radiation from a Van de Graaff generator, the authors were able to calculate a value for $(k_p^2/k_t)^{1/2}$ which they were able to use for estimating the kinetic chain length distribution of the polymerization throughout the substrate.

In a study of the radiation-induced grafting of vinyl monomers to textile fibers by the vapor-phase method, Armstrong (13) has attempted to correlate both the kinetics of the grafting reaction and the diffusion of the monomer into the polymeric fiber. To this stage, however, only the initial phase of this work has been reported, as the effects were found to be complex and could not be represented by simple mathematical solutions.

2. *Grafting with More than One Monomer*

Deviations from normal copolymerization kinetics have also been noted in cases of the direct radiation grafting of more than one monomer to a polymeric substrate.

Consider, for example (see 165), the irradiation of a poly(ethylene) sample immersed in a mixture of styrene and acrylonitrile of a given composition. Both styrene and acrylonitrile would be grafted to the poly(ethylene) as a copolymer of the two. On the basis of the normal copolymer composition equation,

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2}\frac{r_1M_1 + M_2}{r_2M_2 + M_1} \tag{18}$$

where

dM_1/dM_2 = ratio of monomer 1 to monomer 2 in the copolymer formed at any instant

M_1, M_2 = concentrations of monomer 1 and 2, respectively, in the comonomer solution

r_1, r_2 = relative reactivities of monomers 1 and 2, respectively

one should be able to predict the composition of the grafted copolymer provided the values of r_1 and r_2 are known. Odian and co-workers (168) studied the systems styrene–acrylonitrile–poly(ethylene), styrene–methyl acrylate–poly(ethylene), 4-vinylpyridine–styrene–poly(ethylene), methyl acrylate–styrene–poly(tetrafluoroethylene), and acrylonitrile–styrene–poly(tetrafluoroethylene); but in all cases the composition of the graft was not as predicted by the above equation. It was found, for both volumetric and surface grafting, that the more polar of the two monomers (i.e., acrylonitrile, methyl acrylate, and 4-vinylpyridine) was present in the grafted copolymer in an amount greater than predicted. Apparently the reactivity of the more polar monomer in the comonomer mixture is increased in graft copolymerization relative to that in homocopolymerization and/or the reactivity of the less polar monomer is decreased.

The altered reactivities of monomers in the grafting reaction have not been adequately explained but it has been suggested by Odian and Chandler (168) that the gel effect may also alter the value of k_p as well as k_t. Odian further suggests that preferential absorption of the more polar monomer by the growing graft copolymer chain may account for the altered copolymer compositions obtained on grafting.

3. Kinetics in a Homogeneous Preirradiated System

The complicating effects of monomer diffusion and occluded homopolymer on the kinetics of a grafting reaction have been overcome by Turska and Polowinski (285,286) who examined the kinetics of the graft copolymerization of vinyl acetate to preirradiated poly(methyl methacrylate) in a homogeneous system. Both poly(methyl methacrylate) and the graft

TABLE II

Index of Graft Copolymers Prepared by a Radiation Method

Graft copolymers	Ref.	Comments
	1(a) Direct Method	
Amylose-*g*-poly(acrylamide)	336	Kinetics of grafting in aqueous solution
Amylose-*g*-poly(styrene)	347	Grafting in dimethyl sulfoxide solution
Amylose-*g*-poly(vinylpyrrolidone)	337	Effect of grafting on wheat seeds
Cellulose acetate-*g*-poly(acrylamide)	330	Pretreatment of cellulose acetate with methyl vinyl ketone; initiating grafting by reaction of carboxyl with UV light
Cellulose acetate-*g*-poly(acrylonitrile)	85, 268	
	330	Pretreatment of cellulose acetate with methyl vinyl ketone; initiating grafting by reaction of carboxyl with UV light
Cellulose acetate-*g*-poly(styrene)	84, 85	
	87	Composition of graft determined by solvent extraction methods
	139	Mechanical properties, kinetics, mechanisms discussed
	144	Molecular weight distribution measured by sedimentation
	255	
	259	Effect of solvents on grafting reaction investigated
	306	Graft characterized by column elution; fractional precipitation, acid hydrolysis studied
	313	Graft characterized by fractional precipitation, extraction methods
Cellulose acetate-*g*-poly(triallyl citrate)	184	Tensile properties of graft determined
Cellulose acetate-*g*-poly(vinyl acetate)	268	

Cellulose-*g*-poly(acrylamide)	313	Graft characterized by fractional precipitation, extraction methods
Cellulose-*g*-poly(acrylonitrile)	17, 18, 19, 20, 29, 30	Kinetics, structure, physical properties determined
	108, 109	
	119	Mechanical, thermodynamic properties determined
	181, 297	Effect of solvents or graft reaction investigated
	333	Grafting in presence of zinc chloride
Celulose-*g*-poly(butadiene)	324	Grafting kinetics
Cellulose-*g*-poly(butadiene-*co*-acrylonitrile)	224	
	326	Kinetics, properties of grafts studied
Cellulose-*g*-poly(butadiene-*co*-styrene)	224	
Cellulose-*g*-poly(methacrylamide)	119	Mechanical, thermodynamic properties determined
	23	
	109	
Cellulose-*g*-poly(methyl acrylate)	23	Effect of H_2O and MeOH studied
Cellulose-*g*-poly(methacrylate)		Effect of H_2O and MeOH studied, mechanical properties determined
	108	
	216	Effect of presence of water studied
Cellulose-*g*-poly(styrene)	21, 29, 30, 223	
	106	Effect of preswelling cellulose studied
	108, 110	
	118, 218, 297	Effect of solvent on grafting reaction studied
	123	Effect of presence of H_2O and H_2O_2 studied
	126	Structural determination, effect of chain length of properties, ESR study
	145	Effect of swelling agents, mechanical properties determined
	183	Cellulose pretreated with MeOH/HCHO
Cellulose-*g*-poly(styrene)	208, 211	Reaction carried out in presence of air
	281	Physical properties of graft determined
	320	Effect of the presence and absence of water studied

(continued)

TABLE II (*continued*)

Graft copolymers	Ref.	Comments
1(a) Direct Method (continued)		
Cellulose-*g*-poly(styrene)	322	Study of the effect of pretreatment and solvent on grafting
	323	Study of concurrent degradation of the cellulose effect of solvent, oxygen, and other factors
	326	Properties of resulting graft studied
	327	Grafting kinetics
	332	Graft copolymers of bleached jute yarn
	333	Grafting in presence of zinc chloride
Cellulose-*g*-poly(styrene-*co*-butadiene)	326	Kinetics and properties of grafts studied
	326, 327	Grafting kinetics
Cellulose-*g*-poly(styrene-*co*-butadiene-*co*-acrylonitrile)	321	Grafting of ternary mixtures of butadiene, styrene, and acrylonitrile comparison between random and graft copolymerization; regrafting of the graft copolymer; comparison between radiation and popcorn initiation
Cellulose-*g*-poly(vinyl acetate)	23	Effect of H_2O and MeOH on kinetics studied, mechanical properties determined
	333	Grafting in presence of zinc chloride
Cellulose-*g*-poly(2-vinylpyridine)	108	
Cellulose triacetate(methacrylamide)	331	Mechanism of surface grafts under influence of UV light; effect of reaction conditions
Chlorinated poly(vinyl chloride-*g*-acrylonitrile)	302	Thermomechanical properties discussed
Chlorinated poly[(vinyl chloride-*co*-acrylonitrile)-*g*-acrylonitrile]	302	Thermomechanical properties discussed
Chlorinated poly(vinyl chloride-*g*-methyl methacrylate)	353	Kinetics and analyses
Chlorinated poly(vinyl chloride-*g*-styrene)	353	Kinetics and analyses
Chlorinated poly(vinyl chloride-*g*-vinyl acetate)	342	Kinetics, influence of conditions and solvents; some properties discussed

Natural *cis*-1, 4-poly(isoprene-*g*-acrylonitrile)	25	
Natural *cis*-1, 4-poly(isoprene-*g*-methyl methacrylate)	10	Structural characterization, kinetics, mechanisms discussed
	284	
	338	Grafting by sunlight in air
Natural *cis*-1, 4-poly(isoprene-*g*-styrene)	25, 284	
Natural *cis*-1, 4-poly(isoprene-*g*-vinyl chloride)	300	Mechanical properties reported
	362	Influence of solvent and other factors; some properties are discussed
Nylon(6)-*g*-poly(acrylamide)	180	
Nylon(6)-*g*-poly(acrylonitrile)	22	Kinetics, physical properties determined
Nylon(6)-*g*-poly(ethyl acrylate)	257	
Nylon(6)-*g*-poly(methacrylic acid)	199	Grafting carried out in aqueous solution; general physical properties reported
Nylon(6)-*g*-poly(methyl methacrylate)	12	Reaction carried out in MeOH/H_2O solution
	22	Kinetics, physical properties determined
Nylon(6)-*g*-poly(styrene)	12	Reaction carried out in MeOH/H_2O solution
	22	Kinetics, physical properties determined
	180, 226	Accelerating effect of MeOH studied
	274	Effect of ambient gases on kinetics reported
Nylon(6)-*g*-poly(vinyl acetate)	12	Reaction carried out in MeOH/H_2O solution
Nylon(6-6)-*g*-poly(acrylic acid)	134	Effect of graft chain length on properties; molecular weight determination of products
Nylon (6-6)-*g*-poly(maleic acid)	134	Effect of graft chain length on properties; molecular weight determination of products
Nylon(6-6)-*g*-poly(methyl acrylate)	163, 164	Accelerating effect of MeOH studied
Nylon(6-6)-*g*-poly(methyl methacrylate)	172	Accelerating effect of MeOH studied
Nylon(6-6)-*g*-poly(styrene)	25 163, 164, 167, 172, 173	Accelerating effect on MeOH studied
Poly(acrylonitrile-*g*-ethyl acrylate)	83	Effect of acetone on kinetics

(continued)

TABLE II (*continued*)

Graft copolymers	Ref.	Comments
1(a) Direct Method (continued)		
Poly(acrylonitrile-*g*-methyl methacrylate)	186	Reaction carried out in alcoholic solution
Poly[acrylonitrile-*g*-(methyl methacrylate-*co*-vinyl acetate)]	186	Reaction carried out in alcoholic solution
Poly(acrylonitrile-*g*-vinyl acetate)	186	Reaction carried out in alcoholic solution
Poly(acrylonitrile-*g*-vinylpryrrolidone)	129	Effect of inorganic salts on reaction; dyeability improvement
Poly[butadiene(*cis*)-*g*-acrolein]	36	Effect of solvents; grafting also on phosphorylated backbone
Poly[(butadiene-*co*-styrene)-*g*-ammonium acrylate]	360	Grafting of ammonium acrylates and vinyl chelating monomers to rubber latex
Poly[(butadiene-*co*-styrene)-*g*-ammonium methacrylate]	360	Describes formation of a monolayer around a latex particle
Poly[(butadiene-*co*-styrene)-*g*-*N*-(ar-vinyl benzyl) iminodiacetic acid]	360	Describes formation of a monolayer around a latex particle
Poly(butadiene-*g*-methacrylic acid)	343	Kinetics, effect of solvent; some properties discussed
Poly(butyl acrylate-*g*-methyl methacrylate)	81	Study of the effect of the alkyl group on grafting MMA to poly(alkyl acrylates)
Poly(butyl methacrylate-*g*-methyl acrylate)	81	Study of the effect of the alkyl group on grafting MMA to poly(alkyl acrylates)
Poly(butyl methacrylate-*g*-methyl methacrylate)	81	Study of the effect of the alkyl group on grafting MMA to poly(alkyl acrylates)
Poly(caprolactam-*g*-acrylonitrile)	98	Fractional precipitation of products carried out
Poly(caprolactam-*g*-methyl methacrylate)	98	Fractional precipitation of products carried out
Poly(caprolactam-*g*-styrene)	98	Fractional precipitation of products carried out
Poly(cyclohexyl methacrylate-*g*-methyl methacrylate)	81	Study of the effect of the alkyl group on grafting MMA to poly(alkyl acrylates)
Poly(dimethyl siloxane-*g*-acrylonitrile)	58, 65	Kinetics of reaction studied
Poly(dimethyl siloxane-*g*-methyl methacrylate)		

Poly(dimethyl siloxane-*g*-vinylpyrrolidone)	312	Effect of presence of water on kinetics reported
Poly(ethyl acrylate-*g*-acrylonitrile)	82	
Poly(ethylene) blends	335	Graft and block formation in polymer blends, e.g., high and low density poly(ethylene)
Poly[(ethylene-*co*-propylene)-*g*-methyl methacrylate]	359	Preparation and analysis
Poly(ethylene-*g*-acrylonitrile)	25, 39	Kinetics, physical properties discussed
	68	
Poly(ethylene-*g*-alkyl methacrylate)	364	Kinetics of grafting of methacrylates; influences of the length of alkyl chain
Poly(ethylene-*g*-butadiene)	213	
	340	Comparison of kinetics and conditions of vapor and liquid grafting
	346	Comparison of liquid and vapor flow; surface effects
	357	Preparation, analysis, kinetics
Poly[ethylene-*g*-(butadiene-*co*-acrylonitrile)]	213	Effect of MeOH addition studied
Poly[ethylene-*g*-(butadiene-*co*-styrene)]	213	Effect of MeOH addition studied
Poly(ethylene-*g*-*tert*-butylaminoethyl methacrylate)	163, 164	Accelerative effect of *n*-C_6H_{14} reported
Poly(ethylene-*g*-butyl methacrylate)	196	Physical properties reported
Poly(ethylene-*g*-chloroprene)	213	Effect of MeOH addition studied
Poly(ethylene-*g*-isoprene)	213	Effect of MeOH addition studied.
Poly(ethylene-*g*-methacryl glycidyl ester)	358	Improvement of bonding of poly(ethylene) and PTFE with epoxy-based adhesives
Poly(ethylene-*g*-methacrylic acid)	142, 143	Reaction carried out in MeOH; kinetics, mechanisms, effects of storage discussed
	196	Physical properties reported
	356	UV light initiation
Poly(ethylene-*g*-methyl acrylate)	163, 164	Accelerative effect of MeOH studied
Poly(ethylene-*g*-methyl methacrylate)	25	Kinetics, physical properties reported
	44, 68, 71	

(*continued*)

TABLE II (*continued*)

Graft copolymers	Ref.	Comments
	1(a) Direct Method (continued)	
Poly(ethylene-*g*-methyl methacrylate)	74, 76, 172	Effect of solvents and temperature; kinetics discussed
	252	Irradiation carried out in presence of benzoyl peroxide-dimethylaniline
	365	Grafting on poly(ethylene) latex; influence of redox catalyst
Poly(ethylene-*g*-2-methyl-5-vinylpyridine)	272	Irradiation carried out in presence of air
Poly(ethylene-*g*-styrene)	25, 39	Kinetics, physical properties reported
	57	Radiation method compared with chemical-peroxidation method of grafting
	58	Product sulfonated to produce a cation exchange membrane
	68	
	70	Low intensity dose-rates used
	74, 76	Effect of solvents, temperature; kinetics discussed
	78, 102, 247	Kinetics, mechanisms discussed
	163, 164, 169, 170, 171, 172	Accelerative effect of MeOH studied
	211	Effect of organic solvents on grafting efficiency
	347	Low dose-rate grafting, kinetics comparable to emulsion polymerization
	352	Ion exchange membranes of sulfonated grafted poly(ethylene) films
Poly[ethylene-*g*-(styrene-*co*-acrylonitrile)]	39	
	168	Study of monomer reactivities in radiation-induced grafting

Poly[ethylene-*g*-(styrene-*co*-methyl acrylate)]	168	Study of monomer reactivities in radiation-induced grafting
Poly[ethylene-*g*-(styrene-*co*-4-vinylpyridine)]	168	Study of monomer reactivities in radiation-induced grafting
Poly(ethylene-*g*-vinyl acetate)	195, 196	Physical properties determined
Poly(ethylene-*g*-vinylcarbazole)	25	Kinetics, physical properties discussed
	58	Product investigated for use as a high temperature dielectric material
Poly(ethylene-*g*-vinyl chloroacetate)	68	
Poly(ethylene-*g*-vinylidene chloride)	38	Kinetics, physical properties discussed
Poly(ethylene-*g*-vinylpyridine)	25, 196	Kinetics, physical properties discussed
Poly(ethylene-*g*-vinylpyrrolidone)	86	
Poly(ethylene-*g*-vinyl stearate)	25	Kinetics, physical properties discussed
Poly(ethylene terephthalate-*g*-acrylic acid)	11	Physical properties determined
Poly(ethylene terephthalate-*g*-acrylonitrile)	98	Fractional precipitation analysis of products carried out
Poly(ethylene terephthalate-*g*-methyl methacrylate)	98	Fractional precipitation analysis of products carried out
Poly(ethylene terephthalate-*g*-2-methyl-5-vinylpyridine)	11	Physical properties of product determined
Poly(ethylene terephthalate-*g*-styrene)	11, 98	Physical properties, fractional precipitation analysis carried out
Poly(ethylene terephthalate-*g*-4-vinylpyridine)	315	Effect of grafting on dyeability studied
Poly[(isobutene-*co*-isoprene)-*g*-methyl methacrylate]	355	Grafting as function of copolymer composition dose, dose-rate
Poly(isobutylene-*g*-methyl methacrylate)	359	Preparation and analysis
Poly(isobutylene-*g*-styrene)	55	Fractional precipitation analysis of products
	96	Reaction carried out in 50 vol % MeOH
	66	Mechanism of reaction discussed
	231–234	Kinetics of reaction determined; effect of phase separation on kinetics discussed

(*continued*)

TABLE II (*continued*)

Graft copolymers	Ref.	Comments
	1(a) Direct Method (continued)	
Poly(isopropylene-*g*-methyl methacrylate)	81	
Poly(methyl acrylate-*g*-butyl methacrylate)	81	
Poly(methyl methacrylate-*g*-acrolein)	97	Reaction carried out in 40 vol % MeOH
Poly(methyl methacrylate-*g*-acrylonitrile)	93	"Embedded grafting," polymer swollen with monomer in presence of oxygen which inhibits the graft copolymerization to an external zone
Poly(methyl methacrylate-*g*-acrylonitrile)	92, 96	Reaction carried out in 20 vol % MeOH
Poly(methyl methacrylate-*g*-styrene)	153	Product characterized by light scattering
Poly(methyl methacrylate-*g*-vinylpyrrolidone)	96	Reaction carried out in 40 vol % MeOH
Poly(neopentylene-*g*-methyl methacrylate)	81	
Poly(oxymethylene-*g*-methyl methacrylate)	179	Dyeability, thermal stability of product reported
Poly(oxymethylene-*g*-styrene)	179	Dyeability, thermal stability of product reported
Poly(oxymethylene-*g*-vinyl acetate)	179	Dyeability, thermal stability of product reported
Poly(oxymethylene-*g*-vinylpyridine)	179	Dyeability, thermal stability of product reported
Poly(propylene-*g*-acrylic acid)	339	Kinetics; effect of orientation of grafting efficiency
Poly(propylene-*g*-butadiene)	340	Comparison of kinetics; conditions of vapor and liquid grafting
	346	Comparison of liquid and vapor flow surface effects
	357	Preparation, analysis, kinetics
Poly(propylene-*g*-butyl methacrylate)	196	Physical, mechanical properties determined
Poly(propylene-*g*-chloromethyl styrene)	253, 254	Physical, mechanical properties determined
Poly(propylene-*g*-methacrylic acid)	196	Physical, mechanical properties determined
Poly[propylene-*g*-(methacrylic acid-*co*-styrene)]	166	Physical, mechanical properties determined
Poly(propylene-*g*-methyl methacrylate)	172	Accelerative effect of MeOH studied
Poly(propylene-*g*-styrene)	25, 251	Kinetics, physical properties determined
	163, 164, 172	Accelerative effect of MeOH studied
	211	

Poly(propylene-*g*-vinyl acetate)	196	Physical, mechanical properties determined
Poly(propylene-*g*-2-vinylpyridine)	196	Physical, mechanical properties determined
Poly(propylene-*g*-4-vinylpyridine)	196	Physical, mechanical properties determined
Poly(styrene-*g*-acrylonitrile)	299	
	300	Mechanical properties determined
	320	Thermomechanical properties, plasticization of grafts studied; grafts characterized by alkaline hydrolysis
Poly(tetrafluoroethylene-*g*-acrylic acid)	361	Semipermeable membranes by grafting in the mass of PTFE films
Poly(tetrafluoroethylene-*g*-acrylonitrile)	25	Kinetics, physical properties reported
Poly(tetrafluoroethylene-*g*-methacryl glycidyl ester)	308	Improvement of bonding of poly(ethylene) and PTFE with epoxy based adhesives
Poly(tetrafluoroethylene-*g*-methyl acrylate)	163, 164	Accelerative effect of MeOH studied
Poly(tetrafluoroethylene-*g*-methyl methacrylate)	51, 75	Kinetic features discussed
Poly(tetrafluoroethylene-*g*-styrene)	25, 48	Kinetics, physical properties reported
	54	Effect of temperature on grafting studied
	58	Adhesive properties investigated
	75	
	236	Crystallographic study of polymer during grafting
	345	Effect of diffusion and other conditions
	348	Effect of diffusion of styrene in grafting on PTFE
Poly[tetrafluoroethylene-*g*-(styrene-*co*-acrylonitrile)]	166	A comparison of grafting using electron accelerators and isotope sources as radiation initiators was carried out
Poly[tetrafluoroethylene-*g*-(styrene-*co*-methyl acrylate)]	166	A comparison of grafting using electron accelerators and isotope sources as radiation initiators was carried out
Poly(tetrafluoroethylene-*g*-vinyl acetate)	25	Kinetics, physical properties reported
	155	Effect of solvents on grafting; properties of product reported
	191	Kinetic study of the grafting reaction
Poly(tetrafluoroethylene-*g*-vinyl-4-pyridine)	361	Semipermeable membranes by grafting in the mass of PTFE films

(continued)

TABLE II (*continued*)

Graft copolymers	Ref.	Comments
	1(a) Direct Method (continued)	
Poly(tetrafluoroethylene-*g*-*N*-vinylpyrrolidone)	25	Kinetics, physical properties reported
Poly(vinyl acetate-*g*-methyl methacrylate)	176	
Poly(vinyl alcohol-*g*-acrylamide)	241	Improvement in properties discussed
	206	Effect of MeOH on grafting reaction studied
	351	Kinetics and preparation
Poly(vinyl alcohol-*g*-acrylic acid)	206	Effect of MeOH on grafting reaction studied
Poly(vinyl alcohol-*g*-acrylonitrile)	206	Effect of MeOH on grafting reaction studied
	127	Mechanical properties of polymer determined
	227, 228	Effect of solvent studied
	280	Properties of graft reported
	301	
Poly(vinyl alcohol-*g*-allyl methacrylate)	31	Reaction carried out in H_2O/MeOH mixture
Poly(vinyl alcohol-*g*-butadiene)	214	Product characterized by x-ray analysis
Poly[vinyl alcohol-*g*-(butadiene-*co*-styrene)]	214, 224	Product characterized by x-ray analysis
Poly[vinyl alcohol-*g*-(butadiene-*co*-acrylonitrile)]	224	
Poly(vinyl alcohol-*g*-ethyl acrylate)	206	Reaction carried out in MeOH
Poly(vinyl alcohol-*g*-ethyl methacrylate)	206	Reaction carried out in MeOH
Poly(vinyl alcohol-*g*-methyl acrylate)	206	Reaction carried out in MeOH
Poly(vinyl alcohol-*g*-methyl methacrylate)	206	Reaction carried out in MeOH
	127, 280	Physical, mechanical properties determined
	227, 228	Reaction carried out in H_2O/MeOH mixture
	263	Kinetics investigated dilatometrically with periodic irradiation
Poly[vinyl alcohol-*g*-(methyl methacrylate-*co*-vinyl acetate)]	222	Product characterized by x-ray diffraction
Poly[vinyl alcohol-*g*-(5 methyl-2-vinylpyridine)]	206	Reaction carried out in MeOH
	241	Improvement in dyeability of PVA

Poly(vinyl alcohol-*g*-styrene)	127, 280	Mechanical, physical properties reported
	204, 227	Effect of MeOH studied
	228	
	282, 283	Polymer pretreated with H_2O; properties, structure determined
Poly[vinyl alcohol-*g*-(styrene-*co*-acrylic acid)]	222	Product characterized by x-ray analysis
Poly[vinyl alcohol-*g*-(styrene-*co*-acrylonitrile)]	222, 224	Product characterized by x-ray analysis
Poly[vinyl alcohol-*g*-(styrene-*co*-butadiene-*co*-acrylonitrile)]	222	Product characterized by x-ray analysis
Poly[vinyl alcohol-*g*-(styrene-*co*-methacrylic acid)]	222	Product characterized by x-ray analysis
Poly[vinyl alcohol-*g*-(styrene-*co*-methyl methacrylate)]	222	Product characterized by x-ray analysis
Poly(vinyl alcohol-g-vinyl acetate)	206	Reaction carried out in MeOH
Poly(vinyl alcohol-*g*-vinylpyridine)	241	Improvement in properties discussed
Poly(vinyl alcohol-*g*-*N*-vinyl-2-pyrrolidone)	206	Reaction carried out in MeOH
Poly(vinyl chloride-*g*-acrylonitrile)	44, 302	Thermomechanical properties, plastization discussed
	350	Fiber grafts, kinetics, properties
Poly(vinyl chloride-*g*-diallyl esters)	183	
Poly(vinyl chloride-*g*-methacrylic acid)	356	UV light initiation
Poly(vinyl chloride-*g*-methyl methacrylate)	54	Kinetics, effect of solvent discussed
Poly(vinyl chloride-*g*-styrene)	52	Kinetics, effect of solvent discussed
	163, 164, 172	Accelerative effect of MeOH studied
	341	Preparation
	354	Comparison of liquid and vapor phase grafting kinetics
Poly[vinyl chloride-*g*-(styrene-*co*-acrylonitrile)]	53	Kinetics, effect of solvent discussed
Poly(vinyl chloride-*g*-vinyl acetate)	350	Preparation kinetics and properties of grafted fibers
	252	Irradiation carried out in presence of benzoyl peroxide-dimethylaniline
Poly[(vinyl chloride-*co*-acrylonitrile)-*g*-acrylonitrile)]	302	Thermomechanical properties discussed
Poly[(vinyl chloride-*co*-3,3-diphenyl-1-propene)-*g*-acrolein]	363	Sodium naphthalene grafting and UV grafting and crosslinking discussed

(*continued*)

TABLE II (*continued*)

Graft copolymers	Ref.	Comments
	1(a) Direct Method (continued)	
Poly(vinylpyrrolidone-*g*-acrylonitrile)	94	Reaction carried out in 13 vol % benzene
Rayon-*g*-poly(butadiene-*co*-acrylonitrile)	326	Kinetics, properties of grafts studied
Rayon-*g*-poly(butadiene-*co*-styrene)	326	Kinetics, properties of grafts studied
Rayon-*g*-poly(methyl methacrylate)	12	Reaction carried out in H_2O/MeOH solution
Rayon-*g*-poly(styrene)	7	Kinetics, physical properties determined, reaction carried out in presence of air in 1:1 MeOH solution
	12	Reaction carried out in H_2O/MeOH solution
	260	Reaction carried out in presence of air in aqueous solution of a reducing cation
	237	
	326	Kinetics and properties of grafts studied
Rayon-*g*-poly(vinyl acetate)	12	Reaction carried out in H_2O/MeOH solution
Silicon rubber-*g*-poly(vinylpyrrolidone)	312	Applications for product in medical prosthesis work discussed
Silk-*g*-poly(acrylonitrile)	22	Kinetics, dyeability, general properties reported
Silk-*g*-poly(methyl methacrylate)	22	Kinetics, dyeability, general properties reported
	12	Reaction carried out in MeOH/H_2O Solution
Silk-*g*-poly(styrene)	12	Reaction carried out in MeOH/H_2O solution
	22	Kinetics, dyeability, general properties reported
Silk-*g*-poly(vinyl acetate)	12	Reaction carried out in MeOH/H_2O solution
Wood-*g*-poly(methyl methacrylate)	114, 115	Improvement in properties reported
Wood-*g*-poly(styrene)	114	Improvement in properties reported
Wood-*g*-poly(vinyl acetate)	114, 116	Improvement in properties reported
Wool-*g*-poly(acrylonitrile)	103	Reaction carried out in presence of air; physical properties determined
Wool-*g*-poly(methyl methacrylate)	103	Reaction carried out in presence of air; physical properties determined

Wool-*g*-poly(styrene)	103	Reaction carried out in presence of air; physical properties determined

1(b) Direct Vapor Phase Grafting Method

Cellulose-*g*-poly(acrylonitrile)	329	Vapor phase grafting; kinetics, properties of polymers
Cellulose-*g*-poly(butadiene)	14, 15, 16	H_2O, MeOH, HOAc vapors accelerate grafting reaction; physical properties determined
Cellulose-*g*-poly(ethyl acrylate)	14, 15, 16	H_2O, MeOH, HOAc vapors accelerate grafting reaction; physical properties determined
Cellulose-*g*-poly(methyl acrylate)	14, 15, 16	H_2O, MeOH, HOAc vapors accelerate grafting reaction; physical properties determined
Cellulose-*g*-poly(methylstyrene)	329	Vapor phase grafting, kinetics, properties of polymers
Cellulose-*g*-poly(vinyl acetate)	14, 15, 16	H_2O, MeOH, HOAc vapors accelerate grafting reaction; physical properties determined
Cellulose-*g*-poly(vinylidene chloride)	329	Vapor phase grafting; kinetics, properties of polymers
Nylon-(6)-*g*-poly(acrylic acid)	239, 242	Monomer vapor saturated with H_2O; dynamic mechanical properties determined
	303	Describes apparatus for vapor phase grafting
Nylon-(6)-*g*-poly(acrylonitrile)	239, 242	Monomer vapor saturated with H_2O; dynamic mechanical properties determined
	303	Describes apparatus for vapor phase grafting
Nylon-(6)-*g*-poly(butadiene)	303	Describes apparatus
Nylon-(6)-*g*-poly(ethyl acrylate)	239	Monomer vapor saturated with H_2O; dynamic mechanical properties determined
Nylon-(6)-*g*-poly(methyl acrylate)	239, 242	Monomer vapor saturated with H_2O; dynamic mechanical properties determined
Nylon-(6)-*g*-poly(methyl methacrylate)	239	Dynamic mechanical properties determined
	303	Describes apparatus for vapor phase grafting
Nylon-(6)-*g*-poly(styrene)	303	Describes apparatus for vapor phase grafting
Nylon-(6)-*g*-poly(vinyl acetate)	303	Describes apparatus for vapor phase grafting

(continued)

TABLE II (*continued*)

Graft copolymers	Ref.	Comments
1(b) Direct Vapor Phase Grafting Method (continued)		
Plant	366	Description of pilot plant for vapor phase grafting
Poly(ethylene-*g*-acrylic acid)	242	Mechanical properties determined
	303	Apparatus described
Poly(ethylene-*g*-acrylonitrile)	242	Mechanical properties determined
	244, 245	Critical examination of vapor method
	303	Apparatus described
Poly(ethylene-*g*-butadiene)	303	Apparatus described
	340, 346, 357	Comparison of vapor and liquid phase grafting in flowing systems
Poly(ethylene-*g*-ethyl acrylate)	264	Effect of crystallinity studied; product analyzed by x-ray diffraction
	267	Measurements carried out on relation between flow temperature and degree of crystallinity of copolymers
Poly(ethylene-*g*-methyl acrylate)	264	Effect of crystallinity studied
	267	Flow temperature measurements carried out
	242	Mechanical properties determined
Poly(ethylene-*g*-methyl methacrylate)	264	Effect of crystallinity studied; product analyzed by x-ray diffraction
	303	Apparatus described
Poly(ethylene-*g*-styrene)	244, 245	Critical examination of vapor method
	265	Effect of irradiation temperature on grafting studied
	266	Effect of crystallinity determined
	267	Measurements carried out on relation between flow temperature and degree of crystallinity of copolymers

	303	Describes apparatus for vapor phase grafting
Poly(ethylene-*g*-vinyl chloride)	113	Reaction kinetics discussed
Poly(ethylene-*g*-4-vinylpyridine)	264	Effect of crystallinity studied; product analyzed by x-ray diffraction
Poly(ethylene-*g*-vinylidene chloride)	367	Effect of orientation in substrate on orientation in grafted chains
Poly(propylene-*g*-acrylic acid)	303	Describes apparatus for vapor phase grafting
Poly(propylene-*g*-acrylonitrile)	303	Describes apparatus for vapor phase grafting
Poly(propylene-*g*-butadiene)	303	Describes apparatus for vapor phase grafting
	14, 15, 16	H_2O, MeOH, HOAc vapors accelerate grafting reaction; physical properties determined
	340, 346, 357	Comparison of vapor and liquid phase grafting in flowing systems
Poly(propylene-*g*-ethyl acrylate)	14, 15, 16	H_2O, MeOH, HOAc vapors accelerate grafting reaction; physical properties determined
Poly(propylene-*g*-methyl acrylate)	14, 15, 16	H_2O, MeOH, HOAc vapors accelerate grafting reaction; physical properties determined
Poly(propylene-*g*-methyl methacrylate)	303	Apparatus described
Poly(propylene-*g*-styrene)	303	Apparatus described
Poly(propylene-*g*-vinyl acetate)	14, 15, 16	H_2O, MeOH, HOAc vapors accelerate grafting reaction; physical properties determined
	303	Describes apparatus for vapor phase grafting
Poly(tetrafluoroethylene-*g*-acrylonitrile)	244, 245	Critical examination of vapor method
Poly(tetrafluoroethylene-*g*-styrene)	244, 245	Critical examination of vapor method
Poly(vinyl chloride-*g*-acrylonitrile)	244, 245	Critical examination of vapor method
Poly(vinyl chloride-*g*-ethyl acrylate)	264	Effect of crystallinity studied; product analyzed by x-ray diffraction
Poly(vinyl chloride-*g*-methyl acrylate)	264	Effect of crystallinity studied; product analyzed by x-ray diffraction
Poly(vinyl chloride-*g*-methyl methacrylate)	264	Effect of crystallinity studied; product analyzed by x-ray diffraction

(continued)

TABLE II (*continued*)

Graft copolymers	Ref.	Comments
1(b) Direct Vapor Phase Grafting Method (continued)		
Poly(vinyl chloride-*g*-4-vinylpyridine)	264	Effect of crystallinity studied; product analyzed by x-ray diffraction
Poly(vinyl chloride-*g*-styrene)	265, 266	Effect of crystallinity, grafting temperature studied
	354	Comparison of vapor and liquid phase grafting
2. Preirradiation in Air; The Peroxidation Method		
Amylose-*g*-poly(acrylamide)	370	Kinetics and analyses
Cellulose acetate-*g*-poly(methyl methacrylate)	313	Fractional precipitation, solvent extraction used to characterize product
Cellulose acetate-*g*-poly(styrene)	85	Grafting efficiencies of the different radiation methods compared
	87	Composition of product investigated by solvent extraction
	88	Effect of solvents on graft reaction studied
	139, 141	Reaction mechanism, physical properties discussed
	249	Effect of MeOH studied; product characterized by hydrolysis
	306	Reaction carried out in pyridine solution; molecular weight distribution of graft chains determined by column elution, fractional precipitation, acid hydrolysis
	313	Fractional precipitation, solvent extraction used to characterize product
	323	Kinetics, concurrent degradation, composition
Cellulose-*g*-poly(acrylamide)	313	Products characterized by fractional precipitation
Cellulose-*g*-poly(acrylonitrile)	108	The effect of pretreating cellulose with water and/or solvents investigated

Cellulose-*g*-poly(butadiene)	215	Effect of solvents, pretreatment of cellulose discussed
Cellulose-*g*-poly(butadiene-*co*-acrylonitrile)	215	Effect of solvents, pretreatment of cellulose discussed
Cellulose-*g*-poly(butadiene-*co*-styrene)	215	Effect of solvents, pretreatment of cellulose discussed
Cellulose-*g*-poly(methyl methacrylate)	108	Effect of solvents, pretreatment of cellulose discussed
Cellulose-*g*-poly(styrene)	108	Effect of solvents, pretreatment of cellulose discussed
	118, 120	Effect of solvents on reaction investigated
	126	Effect of graft structure on properties discussed; ESR measurements carried out
	145	Effect of swelling agents studied
	161	Monomer added in solvent/H_2O mixture, product characterized by microscopy
	209, 210	Reaction carried out in MeOH–H_2O system
	215	Effect of solvents, pretreatment of polymer discussed
Cellulose-*g*-poly(styrene)	221	Reaction carried out in MeOH–H_2O system; effect of other solvents studied
	332	Styrene grafted on jute yarn; comparison with direct method
	334	Comparison of direct and indirect grafting
Cellulose-*g*-poly(2-vinylpyridine)	108	Effect of solvents, pretreatment of cellulose discussed
Chlorinated poly(vinyl chloride-*g*-acrylonitrile)	299	Mechanical, thermal properties reported
Nylon(6)-*g*-poly(acrylonitrile)	125	Kinetics, mechanisms discussed
	243	Mechanical, thermal properties measured; values correlated to graft structure
	277	Monomer applied to irradiated polymer as an aqueous emulsion
Nylon(6)-*g*-poly(ethyl acrylate)	243	Mechanical, thermal properties measured; values correlated to graft structure
	257	Comparison of various radiation grafting methods
Nylon(6)-*g*-poly(methacrylic acid)	136, 140	Mechanical, thermal properties measured
Nylon(6)-*g*-poly(methyl acrylate)	243	Mechanical, thermal properties measured
	277	Monomer applied to irradiated polymer as an aqueous emulsion

(continued)

TABLE II (*continued*)

Graft copolymers	Ref.	Comments
2. Preirradiation in Air; The Peroxidation Method (continued)		
Nylon(6)-*g*-poly(methyl methacrylate)	243	Mechanical, thermal properties measured
	277	Monomer applied to irradiated polymer as an aqueous emulsion
Nylon(6)-*g*-poly(styrene)	243	Mechanical, thermal properties measured
	277	Monomer applied to irradiated polymer as an aqueous emulsion
Nylon(6)-*g*-poly(vinylpyrrolidone)	277	Accelerative effect of water studied
Nylon(6-6)-*g*-poly(acrylamide)	262	Improvements in general properties reported
Nylon(6-6)-*g*-poly(4-vinylpyridine)	262	Improvements in general properties reported
Poly(acrylonitrile-*g*-acrylamide)	258	Effect of solvent on grafting efficiency studied
Poly(acrylonitrile-*g*-methyl methacrylate)	186	Effect of grafting on properties of polyacrylonitrile fibers studied
Poly(acrylonitrile-*g*-vinyl acetate)	186	Effect of grafting on properties of polyacrylonitrile fibers studied
Poly(caprolactam-*g*-acrylonitrile)	98	Products characterized by fractional precipitation analysis
Poly(caprolactam-*g*-methyl methacrylate)	98	Products characterized by fractional precipitation analysis
Poly(caprolactam-*g*-styrene)	98	Products characterized by fractional precipitation analysis
Poly(ethylene-*g*-acrylic acid)	192, 193, 194	Monomer dissolved in xylene; mechanical, rheological properties of product reported
Poly(ethylene-*g*-acrylonitrile)	35	Kinetics, stability of reactive centers during storage discussed
	47, 50	Influence of preirradiation conditions studied

	86	Reaction kinetics investigated
	151	Effect of redox systems as accelerators discussed
	235	Structure of product determined by x-ray diffraction, electron microscopy
	246	Kinetics of graft reaction reported
	277	Monomer applied to irradiated polymer as an aqueous emulsion
	305	Reaction carried out in DMF
	311	Product hydrolyzed, investigated for use as ion exchange membrane
	373	Effect of air, oxygen, nitrogen, film thickness, temperature, dose-rate, time studied
Poly(ethylene-*g*-alkyl methacrylate)	364	Comparison with direct method of grafting
Poly(ethylene-*g*-ethyl acrylate)	310, 311	Product hydrolyzed investigated for use as ion exchange membrane
Poly(ethylene-*g*-methacrylic acid)	136, 140	Mechanical, thermal properties reported
Poly(ethylene-*g*-methyl acrylate)	240	Mechanical properties determined
	277	Monomer applied to irradiated polymer as an aqueous emulsion
	311	Product hydrolyzed and investigated for use as ion-exchange membrane
Poly(ethylene-*g*-methyl methacrylate)	151	Effect of redox systems as accelerators studied
	235	Structure of product determined by x-ray diffraction, electron microscopy
	240	Mechanical properties reported
	277	Monomer applied to irradiated polymer as an aqueous emulsion
Poly(ethylene-*g*-2-methyl-5-vinylpyridine)	240	Mechanical properties reported
Poly[ethylene-*g*-(propylene-*co*-sulfur dioxide)]	4	Properties determined, method compared with trapped free radical technique
Poly(ethylene-*g*-styrene)	27, 57, 72 75	Kinetics of graft reaction studied

(*continued*)

TABLE II (*continued*)

Graft copolymers	Ref.	Comments
		2. Preirradiation in Air; The Peroxidation Method (*continued*)
Poly(ethylene-*g*-styrene)	111	Kinetics, properties of graft reported
	151	Effect of redox systems as accelerators studied
	202	Influence of inhibitors on graft reaction investigated
	211	Effect of organic solvents on grafting studied
	235	Structure of graft determined by x-ray diffraction, electron microscopy
	240	Mechanical properties reported
	246	Kinetics of graft reaction determined
	277	Monomer applied to irradiated polymer as an aqueous emulsion
	309	Product sulfonated with $ClSO_3H$, investigated for use as ion exchange membrane
	373	Effect of air, oxygen, nitrogen, film thickness, temperature, dose-rate, time studied
Poly(ethylene-*g*-maleic anhydride)	293, 294	Physical properties determined
Poly(ethylene-*g*-vinyl acetate)	235	Structure of graft determined by x-ray diffraction, electron microscopy
Poly(ethylene-*g*-*N*-vinyl-2-pyrrolidone)	240	Physical properties studied
	246	Kinetics of graft reaction determined
	277	Monomer applied to irradiated polymer as an aqueous emulsion
Poly(ethylene terephthalate-*g*-acrylonitrile)	98	Products analyzed by fractional precipitation
Poly(ethylene terephthalate-*g*-methyl methacrylate)	98	Products analyzed by fractional precipitation
Poly(ethylene terephthalate-*g*-styrene)	98	Products analyzed by fractional precipitation
Poly(ethylene terephthalate-*g*-4-vinylpyridine)	104	Mechanism of the graft reaction discussed
Poly(methyl methacrylate-*g*-acrylamide)	35	Kinetics, the stability of the active centers during storage studied

Poly(methyl methacrylate-*g*-acrylonitrile)	230	Polymer irradiated in latex form
Poly(methyl methacrylate-*g*-styrene)	153	Product characterized by light scattering
	278	Mechanism of graft reaction studied; graft efficiency measured by fractional precipitation
	285	Kinetic study of the graft reaction
Poly(methyl methacrylate-*g*-vinyl acetate)	286	Kinetic study of the graft reaction
Poly(methyl methacrylate-*g*-vinylpyrrolidone)	122	Mechanism discussed, effect of temperature, dose-rate studied
	130	Kinetic study of the graft reaction
Poly(oxymethylene-*g*-methyl methacrylate)	179	Effect of reaction variables studied
Poly(oxymethylene-*g*-styrene)	179	Effect of reaction variables studied
Poly(oxymethylene-*g*-vinyl acetate)	179	Effect of reaction variables studied
Poly(oxymethylene-*g*-vinylpyridine)	179	Effect of reaction variables studied
Poly(propylene-*g*-acrylamide)	3	Kinetics, effects of presence of metallic salt during irradiation studied
Poly(propylene-g-acrylic acid)	174	Kinetics, improvements in dyeability reported
	276	Kinetics, effects of the addition of salts on surface-active agents studied
	307, 308	Reaction carried out in MeOH solution, structure determined by x-ray measurements; thermal, mechanical properties discussed
Poly[propylene-*g*-(acrylic acid-*co*-styrene)]	276	Kinetics, effects of the addition of salts on surface-active agents studied
Poly(propylene-*g*-acrylonitrile)	47, 50, 51	Influence of preirradiation conditions on kinet'cs of graft reaction studied
	151	Effect of redox systems as accelerators discussed
	174	Kinetics, improvements in dyeability reported
	250	Kinetics of graft reaction studied
	277	Monomer applied to irradiated polymer as an aqueous emulsion

(continued)

TABLE II (*continued*)

Graft copolymers	Ref.	Comments
2. Preirradiation in Air; The Peroxidation Method (continued)		
Poly(propylene-*g*-acrylonitrile)	307	Reaction carried out in MeOH solution, structure determined by x-ray measurements; thermal, mechanical properties discussed
	308	Graft reaction carried out in presence of ferrous sulfate to give a product with less homopolymer
Poly[propylene-*g*-maleic anhydride-*co*-acrylonitrile)]	296	
Poly[propylene-*g*-(maleic anhydride-*co*-2-methyl-5-vinylpyridine)]	296	
Poly[propylene-*g*-(maleic anhydride-*co*-vinyl acetate)]	296	
Poly(propylene-*g*-methyl acrylate)	240	Physical properties studied
	277	Monomer applied to irradiated polymer as an aqueous emulsion
Poly(propylene-*g*-methyl methacrylate)	3	Kinetics, effects of presence of metallic salt during irradiation studied
	151	Effect of redox systems as accelerators discussed
	174	Kinetics, improvements in dyeability reported
	240	Physical properties studied
Poly(propylene-*g*-2-methyl-5-vinylpyridine)	240	Physical properties studied
	307	Reaction carried out in MeOH solution, structure determined by x-ray measurements; thermal, mechanical properties discussed
	308	Graft reaction carried out in presence of ferrous sulfate to give a product with less homopolymer
Poly(propylene-*g*-propylene)	377	Kinetics and conditions studied
Poly(propylene-*g*-styrene)	112	Kinetics, mechanical properties investigated

	151	Effect of redox systems as accelerators discussed
	211	Influence of organic solvents in grafting step
	240	Physical properties studied
	277	Monomer applied to irradiated polymer as an aqueous emulsion
Poly[propylene-*g*-(styrene-*co*-diethyl fumurate)]	296	
Poly[propylene-*g*-(styrene-*co*-fumaric acid)]	296	
Poly[propylene-*g*-(styrene-*co*-itaconic anhydride)]	296	
Poly[propylene-*g*-(styrene-*co*-maleic acid)]	296	
Poly[propylene-*g*-(styrene-*co*-maleic anhydride)]	293, 294, 296	Physical properties studied
Poly[propylene-*g*-(styrene-*co*-sulfur dioxide)]	220	Physical properties studied
Poly(propylene-*g*-vinyl acetate)	174	Kinetics, improvement in dyeability
	240	Physical properties studied
	273, 275	Graft reaction carried out in an emulsion system; mechanical, thermal properties, dyeability examined
	307	Structure of graft determined by x-ray diffraction; thermal, mechanical properties reported
	308	Graft reaction carried out in presence of ferrous sulfate to give a product with less homopolymer
Poly(propylene-*g*-vinyl caprolactam)	174	Kinetics, improvements in dyeability reported
Poly(propylene-*g*-vinylpyridine)	174	Kinetics, improvements in dyeability reported
Poly(propylene-*g*-vinylpyrrolidone)	277	Accelerative effect of H_2O studied
Poly(tetrafluoroethylene-*g*-methyl methacrylate)	124	Polymer irradiated by silent discharge
Poly(tetrafluoroethylene-*g*-styrene)	72	Grafting reaction followed dilatometrically
Poly(vinyl alcohol-*g*-acrylamide)	206	Reactivity of several vinyl monomers to peroxidation grafting compared
Poly(vinyl alcohol-*g*-acrylic acid)	206	Reactivity of several vinyl monomers to peroxidation grafting compared
Poly(vinyl alcohol-*g*-acrylonitrile)	206	Reactivity of several vinyl monomers to peroxidation grafting compared

(continued)

TABLE II (*continued*)

Graft copolymers	Ref.	Comments
		2. Preirradiation in Air; The Peroxidation Method (*continued*)
Poly(vinyl alcohol-*g*-ethyl methacrylate)	206	Reactivity of several vinyl monomers to peroxidation grafting compared
Poly(vinyl alcohol-*g*-methyl acrylate)	206	Reactivity of several vinyl monomers to peroxidation grafting compared
Poly(vinyl alcohol-*g*-methyl methacrylate)	206	Reactivity of several vinyl monomers to peroxidation grafting compared
	127	Effect of inorganic salts on graft reaction studied
	217	Product characterized by hydrolysis
	225	Structure of graft analyzed by fractional precipitation, hydrolysis techniques
Poly(vinyl alcohol-*g*-5-methyl-2-vinylpyridine)	206, 207	Reactivity of several vinyl monomers to peroxidation grafting compared
Poly(vinyl alcohol-*g*-styrene)	127	Effect of inorganic salts on graft reaction studied
	205, 207	Effect of temperature on graft reaction studied
Poly(vinyl alcohol-*g*-vinyl acetate)	206	Reactivity of several vinyl monomers to peroxidation grafting compared
Poly(vinyl alcohol-*g*-*N*-vinyl-2-pyrrolidone)	206	Reactivity of several vinyl monomers to peroxidation grafting compared
Poly(vinyl chloride-*g*-acrylonitrile)	314	
	376	Kinetics and analyses; optimum conditions established
Rayon-*g*-poly(acrylonitrile)	216	Effect of presence of solvent, pretreatment of polymer studied
	277	Monomer applied to irradiated polymer as an aqueous emulsion
Rayon-*g*-poly(methyl acrylate)	277	Monomer applied to irradiated polymer as an aqueous emulsion

Rayon-*g*-poly(methyl methacrylate)	277	Monomer applied to irradiated polymer as an aqueous emulsion
Rayon-*g*-poly(styrene)	216	Effect of presence of solvent studied
	219	Effect of solvents on kinetics, mechanical properties of graft reported
	277	Monomer applied to irradiated polymer as an aqueous emulsion
Rayon-*g*-poly(vinylpyrrolidone)	277	Monomer applied to irradiated polymer as an aqueous emulsion

3. Preirradiation in vacuo; Trapped Free Radical Technique

Amylose-*g*-poly(acrylamide)	152	
Cellulose-*g*-poly(acrylonitrile)	17, 20	Effect of radiation on cellulose discussed; structure, properties of graft reported
Cellulose-*g*-poly(styrene)	17, 20	Effect of radiation on cellulose discussed; structure, properties of graft reported
	117	Build-up, decay of radicals followed by ESR; kinetics of graft reaction studied
	320	Effect of moisture, pretreatment, drying procedures
	325	Effect of process of oxygen
	327	Effect of temperature, humidity, storage time on grafting
Nylon(6)-*g*-poly(ethyl acrylate)	257	Grafting efficiency very poor
Nylon(6)-*g*-poly(acrylonitrile)	32	Kinetics, mechanism of graft reaction followed by using C^{14}-labeled monomer
Poly(acrylonitrile-*g*-acrylonitrile)	32	Kinetics, mechanism of graft reaction followed by using C^{14}-labeled monomer
Poly(acrylonitrile-*g*-ethyl acrylate)	83	
Poly(ethylene-*g*-acrylonitrile)	158	Effect of varying reaction, irradiation conditions discussed

(*continued*)

TABLE II (*continued*)

Graft copolymers	Ref.	Comments
3. Preirradiation in vacuo; Trapped Free Radical Technique (continued)		
Poly[ethylene-*g*-(1-hexene-*co*-sulfur dioxide)]	375	Grafting kinetics and analysis
Poly[ethylene-*g*-(propylene-*co*-sulfur dioxide)]	4	Method compared with preirradiation in air technique; properties of graft determined
Poly(ethylene-*g*-styrene)	8	Properties of graft investigated, compared with and corresponding physical blend of poly(styrene) and poly(ethylene)
	27	Kinetics of graft reaction studied
	211	Effect of organic solvents on graft reaction investigated
	309	Product sulfonated with ClSO$_3$H, investigated for use as ion exchange membrane
	372	Effect of time and environment on radical decay
Poly(ethylene terephthalate-*g*-acrylonitrile)	32	Kinetics, mechanism of graft reaction followed by using C^{14}-labeled monomer
Poly(methyl methacrylate-*g*-styrene)	153	Method compared with peroxidation technique
Poly(propylene-*g*-acrylonitrile)	158	Effect of varying reaction, irradiation conditions discussed
Poly[propylene-*g*-(1-hexene-*co*-sulfur dioxide)]	375	Grafting kinetics and analysis
Poly(propylene-*g*-styrene)	211	Effect of organic solvents on graft reaction investigated
	371	Use of secondary radiation, kinetics of grafting
	374	Effect of structure and environment on grafting kinetics
Poly(propylene-*g*-vinylpyrrolidone)	374	Effect of structure and environment on grafting kinetics
Poly(styrene-*g*-acrylonitrile)	32	Kinetics, mechanism of graft reaction followed by using C^{14}-labeled monomer

Poly(tetrafluoroethylene-*g*-styrene)	201	Kinetics discussed, product examined microscopically
	369	Gas phase grafting kinetics
Poly(vinyl alcohol-*g*-styrene)	205	Effect of varying reaction conditions reported
Poly(vinyl chloride-*g*-styrene)	205	Effect of varying reaction conditions reported
Silica gel-*g*-poly(acrylic acid)	368	Ion exchange sorbent from organo mineral nature
Silica gel-*g*-poly(styrene)	368	Ion exchange sorbent from organo mineral nature
	4. Intercrosslinking Method	
Poly(vinyl chloride-*g*-vinylpyridine)	1	Both polymers dissolved in tetrahydrofuran; the solution irradiated at room temperature
Poly(vinylpyrrolidone-*g*-acrylamide)	91	Polymers dissolved in aqueous solution, irradiated at room temperature; mechanism of the reaction discussed
	5. Emulsion Techniques	
Natural *cis*-1,4-poly(isoprene-*g*-methyl methacrylate)	59, 60	Film-forming properties of product compared with graft made by chemical initiation
	62, 64	Kinetics of graft reaction studied
	63	Molecular weight distribution of products determined using column fractionation
Natural *cis*-1,4-poly(isoprene-*g*-styrene)	61	Advantages of radiation emulsion grafting discussed; reaction rates, etc. compared with MMA case
Poly(butyl methacrylate-*g*-styrene)	89	Investigation of the efficiency of the emulsion technique; products separated by fractional precipitation
Poly(butyl methacrylate-*g*-vinyl acetate)	89	
Poly(ethyl acrylate-*g*-methyl methacrylate)	90	Mechanism discussed together with investigation of efficiency of the process; product separated by fractional precipitation
Poly(methyl acrylate-*g*-ethyl acrylate)	90	
Poly(methyl methacrylate-*g*-acrylonitrile)	90	

(continued)

TABLE II (*continued*)

Graft copolymers	Ref.	Comments
	5. Emulsion Techniques (*continued*)	
Poly(methyl methacrylate-*g*-styrene)	2	Kinetics discussed; homopolymer separated by thermal elution chromatography
Poly(methyl methacrylate-*g*-vinyl acetate)	89	Investigation of efficiency of emulsion technique; products separated by fractional precipitation
Poly(styrene-*g*-methyl methacrylate)	89	
	2	Kinetics discussed; homopolymer separated by thermal elution chromatography
Poly(tetrafluoroethylene-*g*-butyl methacrylate)	90	Mechanism discussed together with investigation of efficiency of the process; products separated by fractional precipitation
Poly(tetrafluoroethylene-*g*-ethyl acrylate)	90	
Poly(tetrafluoroethylene-*g*-methyl methacrylate)	90	
Poly(tetrafluoroethylene-*g*-styrene)	90	
Poly(tetrafluoroethylene-*g*-vinyl acetate)	90	
Poly(vinyl acetate-*g*-acrylonitrile)	89	Investigation of efficiency of emulsion technique; products separated by fractional precipitation

copolymer formed in the process are soluble in the monomer and the reaction can thus be carried out in a one-phase system. The rate of reaction for low conversion was found to be proportional to the concentration of the monomer raised to the power of $^3/_2$ and to the concentration of initiator to the $^1/_2$ power. The reaction was found to be in good agreement with the kinetic equation for ordinary addition polymerization if the decrease of the amount of initiator during the process was taken into consideration.

The work of Turska and Polowinski represents an almost ideal case which one does not encounter in most grafting systems. It can be seen then, that while weight gain data on "extracted" polymers may give some idea of the general mechanism of the graft reaction, accurate and reliable kinetic data cannot be obtained unless a method of grafting is developed which yields 100% graft with no occluded homopolymer or when more sophisticated characterization techniques are employed. Surprisingly, this situation was realized quite early by Shashoua and Van Holde (378). These authors developed a method of preparing 100% grafted polymers by a two-state emulsion polymerization process involving the use of crosslinked microgels. The polymers were analyzed as microsols by limiting viscosity number and by ultracentrifugation measurements. It has only been quite recently, however, that this type of grafting process has been employed in a kinetic study of radiation-induced grafting. Matsuda and co-workers (through 247) have reported grafting of styrene to gelated poly(ethylene) and, although detailed results have not as yet been published, the use of gelated systems in the study of kinetics appears to have good merit.

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IV. PROPERTIES OF BLOCK AND GRAFT COPOLYMERS

It is often assumed that block and graft compositions have valuable properties and that commercial exploitation is held up by the lack of suitable, low cost methods of synthesis. This may be true in part but even now surprisingly little detail is known about the properties of these copolymers with relation to known structures or for that matter to the unknown heterogeneous structures produced by most methods of synthesis. The following sections are specifically directed toward an understanding of the physical and structural properties featured by grafts. Making a broad generalization based on this review it is suggested that certain block and graft structures may have useful properties.

The commercial value of graft copolymers (and blocks for that matter, treated as a special case of the grafted polymer family) depends to a great extent on whether they offer advantages over physical blends. Close relationship and overlap exist between the two types and these are apparent in several of the commercial graft materials for which counterparts are made by blending. The overlap is particularly confusing in the case of high impact poly(styrene), because of the unusual physical blend arising in the graft product.

Generally, a block or graft copolymer should offer clear advantages over a physical blend when a high degree of incompatibility exists between the component parts. It is difficult to make a well dispersed blend of polymers which have poor solubility in one another. Even when this can be done, migration and separation will occur under stress because of poor adhesion and the combination will have low strength properties. The mutual solubility of components will be of the same order in a block, graft, or physical mixture. Because they are tied in a copolymer by chemical bonds, however, the components will necessarily be in a highly dispersed state and will be prevented from separating, or may in turn give rise to organized structure.

The properties of grafts will, of course, vary according to the degree of segregation of monomer units, i.e., according to the number and length of segments. As the segmented length decreases, properties of grafts will approach those of random copolymers. However, assuming the molecule contains only a few grafted segments, the natural solubility of the copolymer components will have a decisive influence on properties. According to whether the components are more or less soluble in each other, the copolymer will exhibit more or less distinctly two sets of properties similar to those of the corresponding homopolymers. Three cases can be considered; first, insoluble or highly insoluble components; secondly, component B soluble in amorphous phase of crystalline component A, and finally, soluble components. Keeping this general outline in mind, the properties of graft copolymers and structural features will be discussed in the following section in a more fundamental and detailed form.

1. SOLUTION PROPERTIES*

A. General

Most molecular parameters of polymers are measured through the properties of dilute solutions. The theory of the thermodynamic properties of dilute polymer solutions, which was independently developed by P. J. Flory and M. L. Huggins (for a brief treatment of this theory see references (1,2)) and extended by many others, has proven useful in interpreting, qualitatively and semiquantitatively, the behavior of both dilute and nondilute solutions and also in the determination of average molecular weights and dimensions from experimental data in leading to the so-called "interaction constants" (characteristic of the polymer–solvent system), and in many other ways. It had, however, inherent limitations particularly if specific interactions occurred between polymer molecules, or the polymer–solvent system increased in complexity. This failure of the dilute solution thermodynamics is evident when graft copolymers are considered. Again, Huggins (3) attempted to cover this area with a tentative set of equations which as yet cannot be used.

The situation is indeed extremely complicated. If a graft copolymer is prepared by one method or another, not only the graft copolymer sought is obtained but the corresponding homopolymers as well. Furthermore, the composition of the grafted molecules may vary considerably without taking molecular weight into consideration (Smets, 5; Chapiro, 6; Franta, 7). In the case of homopolymers we have, ideally, linear molecules which vary only in length, but in the case of block and graft copolymers we have a mixture where the species differ in molecular weight, composition, and structure. Such analytical methods as precipitation or dissolution fractionation, so successful for linear homopolymers, become nearly impossible for graft and block copolymers since all three variables—molecular weight, composition, and structure—influence fractional solubility (see, for example, Burnett, 8; Mita, 9; Krause, 10). To add to the predicament it was found that graft copolymers are often insoluble (Danon, 11) in the solvents of either corresponding homopolymeric component. It is therefore logical to deal first with the solubility behavior per se before proceeding to the description of the properties of dilute solution and the derived molecular parameters.

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*References for this subsection will be found on pages 129–130.

B. Solubility of Graft Copolymers

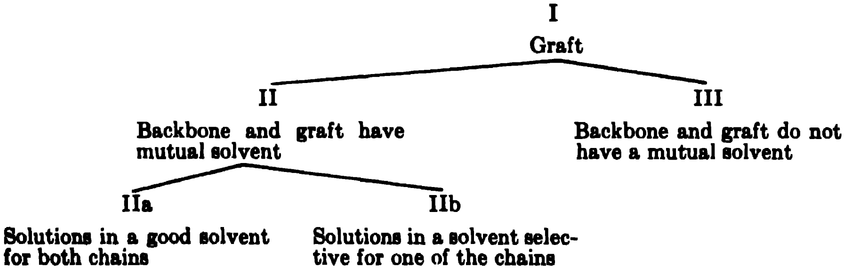
1. General

The interaction of solvents with block and graft copolymers is a complex phenomenon strongly dependent upon composition and structure of the species. Blocks and grafts should be treated simultaneously since a block copolymer, in the simplest form, is a type of graft copolymer with the graft chain tagged on to the end of the backbone. Poly(methyl methacrylate-*b*-styrene) has been used as an example of how solubility and viscosity can help characterize the polymer (O'Driscoll et al., 12). In the random copolymerization of styrene with methyl methacrylate in the presence of lithium it was found that for an extraction of a copolymer containing 90% methyl methacrylate using acetonitrile (a selective solvent for poly(methyl methacrylate) but not for poly(styrene)), a soluble fraction was obtained containing less than 10% styrene. This fraction cannot be poly(styrene), nor a random copolymer, and since it was insoluble in cyclohexone, a solvent for poly(styrene) but not for random copolymers of poly(styrene), a block copolymer was postulated consisting of poly[methyl methacrylate-*b*-(styrene-*co*-methyl methacrylate)]. These authors also indicated the occurrence of "opaque" solutions, colloidal dispersions of the block copolymer protected in suspension by its own structure (O'Driscoll, 13). This is one of the many examples that may be chosen to demonstrate the solubility behavior of grafts and blocks.

An interesting example was given by Merrett (14,15) particularly since the products involved have found industrial use (Hevea Plus, 16). A benzene solution of rubber grafted by methyl methacrylate yields a colloidal solution when either methanol or petroleum ether is added. It was proposed by Merrett that the poly(methyl methacrylate) grafted chains remain extended while the rubber backbone "collapses" in the former case, the reverse occurring in the latter. If the solvent is evaporated from these two solutions, materials are obtained resembling poly(methyl methacrylate) and rubber, respectively.

The same type of behavior was observed by Bresler for poly(styrene-*b*-isoprene) while the authors of this volume (18) observed similar properties for poly(vinyl chloride-*g*-methyl methacrylate), poly(vinyl chloride-*g*-ethyl acrylate), and poly(vinyl chloride-*g*-vinyl acetate). Climie (23) reported not only the virtual phase separation for a block copolymer poly(methyl methacrylate-*b*-acrylonitrile) in solvents selective for either partner in the block, but also a time effect.

It is evident that the solution behavior of graft copolymers is not a simple function of the corresponding solubilities of the homopolymers. The most interesting and utilitarian effects are obtained with dissimilar backbone and graft chains and solvent mixtures that are selective. Classification can be based on the following scheme (Benoit, 24).


I
Graft
II
Backbone and graft have mutual solvent
III
Backbone and graft do not have a mutual solvent
IIa
Solutions in a good solvent for both chains
IIb
Solutions in a solvent selective for one of the chains

Several attempts have been made to arrive at a model of the solubility behavior exemplified above.

2. Thermodynamic Treatment

A number of authors have attempted to give a thermodynamic treatment of dilute graft solutions, since it is obvious that the behavior of these solutions cannot be described by the Flory-Huggins theory.

Kilb and Bueche (25), starting with the Flory (2) lattice model and Stockmayer's (26) treatment thereof for random copolymers and derived the following expression for the free energy of mixing of a graft copolymer with a solvent,

$$\Delta F_m = kT[n \ln(\nu_A + \nu_B) + n_S \ln \nu_S + \chi_A n_A \nu_A + \chi_B n_S \nu_B] \qquad (1)$$

where

ν_A, ν_B, and ν_S	are the volume fractions of polymer A ,B, and solvent S (volume fraction of graft polymer is then $\nu_A + \nu_B$)

k and T	are the Boltzman's constant and absolute temperature, respectively
χ_A and χ_B	are dimensionless quantities which characterize the interaction energy of a solvent molecule with polymer A and B
n_S and n	are the number of solvent and graft molecules, respectively

The graft polymer is assumed to be composed of x segments of polymer A and y segments of polymer B. The x and y segments are not the monomer units but are taken such that their volume is equal to the volume of a solvent molecule.

Polymer molecules will enter solution as long as the corresponding change in free energy is negative, i.e., if the partial molar free energy of mixing is negative.

$$\frac{1}{kT}\frac{\partial \Delta F}{\partial n} = \ln(\nu_A + \nu_B) - (x + y - 1)\nu_S + \nu_S^2(x\chi_A + y\chi_B) \qquad (2)$$

The first two terms arise from the entropy effect. They are always negative and thus always favor solution of the polymer. The solubility is therefore controlled by the heat of interaction term $\nu_S\,(x\chi_A + y\chi_B)$. If $(x\chi_A + y\chi_B)$ is negative (i.e., if heat is given off on dissolving the polymer), then the polymer is soluble in all proportions. If the polymer and solvent are nonpolar, χ_A and χ_B will be positive. The solubility may therefore be limited and it decreases as χ_A and χ_B increase. In this case solubility can be gauged by the Hildebrand (28) solubility parameters. If, however, polar interaction or hydrogen bonding occurs, as in the case of PVC (Small, 29; Adelman, 30), the above relation will break down.

Bueche's formula in the form given is only useful as a qualitative guide. As the solubility will increase as χ_A and χ_B increase, solubility in a particular type of solvent can be decreased or increased by regulating χ_B of the grafted chain accordingly. In general, grafting will decrease solubility, since the entropy term is only weakly dependent on the nature of the graft, but the heat term is sharply influenced. This is opposed to the general rule found by Beaman and Cramer (31) for random copolymers, predicting an increase in solubility.

Krause (27) modified the Bueche equation to

$$\Delta F_m = kT[n \ln \nu_p + n_S \ln \nu_S + \chi_p n_S \nu_p] \qquad (3)$$

and

$$\chi_p = \chi_{AS}\,\nu_A{}^p + \chi_{BS}\,\nu_B{}^p - \chi_{AB}\,\nu_A{}^p\,\nu_B{}^p \tag{4}$$

where the symbols have now the more conventional meaning in the Flory (2) notation:

χ_p	the interaction constant for graft copolymer with solvent
$\chi_{AS}\chi_{BS}\chi_{AB}$	interaction constants for components of the system
$\nu_A{}^p\nu_B{}^p$	volume fractions of monomer units A and B in the graft copolymer

Equation 3 is now identical in form with the equation obtained by Scott for the free energy of mixing for two homopolymers in a single solvent. The interaction constant for a polymer mixture χ_M'' may then be expressed as

$$\chi_M = \chi_{AS}\,\nu_A{}^p + \chi_{BS}\,\nu_B{}^p + \chi_{AB}\,\nu_A{}^p\,\nu_B{}^p\left(\frac{\nu^p}{\nu_S}\right) \tag{5}$$

which is concentration dependent, and is difficult to use for further calcluation. Stockmayer's (26) expression for the interaction constant for a binary random copolymer and a solvent can be written as

$$\chi_p = \nu_A\chi_{AS} + \nu_B\chi_{BS} - \nu_A\nu_B\chi_{AB} \tag{6}$$

However, Stockmayer clearly postulates that in eq. 6, χ_{AB} is not the same as in eq. 4, since in a random copolymer the assumption of chain segments of sufficient length to compare with the solvent is not always possible. It was not surprising then that eq. 6 was found to fail. This is particularly clear in the case of the empirical rule quoted earlier: grafts are, in general, less soluble than the corresponding homopolymers, which in turn are less soluble than the corresponding random copolymer.

Danon (11) approached the solubility problem from the point of view of the solubility parameter δ of the Scatchard-Hildebrand theory (28). He made calculations for two limiting cases.

1. The two homopolymers corresponding to the backbone and grafted side chains of the graft copolymer are completely miscible. Then

$\delta_A = \delta_B$ and/or the branches are very short.

2. The two polymers A and B are completely immiscible, or $p = \delta_A - \delta_B$ is large and the chain types A and B in the graft are long.

For the first case Danon postulates

$$\delta_g = [(1 - \beta)\delta_A + \beta\delta_B] \tag{7}$$

This is similar to the Scatchard-Magat equation for mixed solvents, where δ's are the solubility parameters for the graft copolymer and the corresponding homopolymers, and

$$\beta = \frac{\nu_A}{\nu_A + \nu_B} \tag{8}$$

the grafting ratio expressed as a molar volume ratio.

Equations 7 and 8 are still valid when the system has two coexisting phases, conditional, however, on uniformity of the graft.

In the second case, which, unfortunately, applies to most graft copolymers, when the polymer constituents are incompatible in the solid state as well as in solution, no simple relations can be established. At all times the two types of polymer chain are participants in two microphases (Sadron, 20). With some very severe simplifications (and consequently limitations) Lautout and Magat (34) assuming that the solvent partitions between the chains A and B is proratio of $\beta/1 - \beta$, derived for the heat of mixing ΔH_m

$$\Delta H_m = V_m[(\delta_0 - \delta_A)^2(1 - \beta) + (\delta_0 - \delta_B)^2\beta]\nu_p\nu_0 \tag{9}$$

while for the first case Danon found

$$\Delta H_m = V_m\{\delta - [(1 - \beta)\delta_A + \beta\delta_B]\}^2\nu_p\nu_0 \tag{10}$$

Equation 7 is obvious from eq. 10 but eq. 9 does not allow a simple substitution of a δ_g.

By the usual thermodynamic manipulations the critical miscibility can be calculated for a given set of conditions (Tompa, 35). Plotting the solubility limits as a function of β for various values of $p = \delta_A - \delta_B$, Danon obtained Figs. 1 and 2.

Lautout and Magat (34) developed some expressions of interest, later modified by Danon (11). A condensed version is given here because the treatment of copolymer solubility proposed, in essence, describes the behavior of a particular class of graft copolymers rather well. Based on earlier work (32,33, 40) the critical heat of mixing for a statistical copolymer can be expressed as

$$\Delta H_c = \frac{V_m}{RT}\{\delta_0 - [\delta_A\beta + \delta_B(1 - \beta)]\}^2 = \frac{1}{2} - \frac{1}{Z} = 0.22$$

for very high molecular weight, when V_m is the molecular volume for the polymer and β is the volume fraction of monomer A, Z being a coordinate number. This relation was tested quantitatively for poly(butadiene-*co*-styrene) and poly(butadiene-*co*-acrylonitrile) and found to be accurate for the first copolymer, but showed deviation for the latter due to the polarity of the acrylonitrile group. Given $RT = 600$ cal and $Vm = 100$ cc (a good average for a high molecular weight polymer), one obtains

$$|\delta_0 - \{\delta_A\beta + \delta_B(1 - \beta)\}| \leq 1.16 \tag{11}$$

If we take by definition $\delta_A > \delta_B$ and $\delta_A - \delta_B = p$ and

$$|\delta_0 - \delta_A| = \Delta\delta_A, \ \Delta\delta_A + p(1 - \beta) \leq 1.16 \tag{12}$$

Plotting $\Delta\delta_A$ as a function for β for various values of p we obtain Fig. 1 with critical values falling as straight lines passing through $\delta_A = +1.16$ for $\beta = 0$ and $\delta_A = -1.16$ for $\beta = 1$. Thus solvents can be found for copolymers of the whole composition range. Within the same approximations adapted for the random copolymer, but taking into account that segment volumes for each type of chain are different (excepting the case of a large number of short grafted chains) one can again assign a composite solubility parameter to the graft copolymer

$$\delta_g = \delta_A\beta + \delta_B(1 - \beta) \tag{13}$$

being simply the arithmetic sum for the composing polymers. This equation applies when the corresponding homopolymers have solubility parameters answering the relation

$$\Delta\delta_A + p(1 - \beta) \leq 1.16$$

This condition is usually associated with polymers compatible in solution. Figure 1 again expresses the critical solution conditions graphically. It is known, however (42, for example), that most polymers are incompatible in solid blends as well as in solution. The initial thought comes to mind that for

$$p = |\delta_B - \delta_A| \geq 1 \tag{14}$$

separation into two phases should occur in solution, but on microscopic or molecular level, each "phase" consisting of one molecular chain with solvent. In the following treatment Magat made (serious) simplifications;

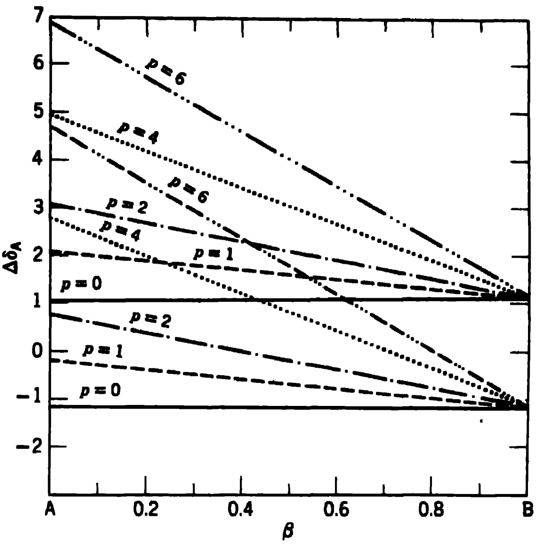


Fig. 1. Phase relationship in graft copolymers solutions (11). Case 1: $\delta_A = \delta_B$.

the amount of solvent in each phase is proportional to the volume fractions of chains A and B. This is only the case, however, when

$$(\nu_0 - \nu_A)^2 = (\nu_0 - \nu_B)^2$$

However, the mathematical treatment becomes too cumbersome when the partition of the solvent is taken into account.

The free energy equation obtained does not allow a simple mathematical expression for δ_g but has, however, two real solutions if

$$p^2(1 - \beta)\beta \leq \left(\frac{1}{2} - \frac{1}{Z}\right)\frac{V_0}{RT} \qquad (15)$$

Thus, for certain high values of $p = \nu_A - \nu_B$ *and for certain values of* β, *graft (and block) copolymers are insoluble.*

Taking again the same numerical values used earlier ($1/Z = 0.28$, $V_0 = 100$ cc, $T = 293$°K, $R = 1.90$° cal/deg a plot can be made of the critical solubility as a function of ν_A and β for various values of p.

A domain of complete insolubility applies for given compositions when there is no common solvent which can dissolve either corresponding homopolymers, taken singly. With the numerical values given, and for

$$p = \delta_A - \delta_B > 2.28 \tag{16}$$

a single point occurs for $\beta = 0.5$, $p = 2.28$, $\Delta\delta_A = 1.14$ when molecular weights are very high and partition of the solvent takes place according to the ratio $\beta/1 - \beta$.

In practice, however, to obtain values of 2.28, polymers need to be polar, when the equations presented based on the Scatchard–Hildebrand principle cannot be applied any more. However, a number of these phase separations have been reported and form an important field of application of graft copolymers. This subject will be dealt with in a later section.

Danon (11) applied these equations to the following polymer systems:

	p
poly(vinyl chloride-*g*-acrylonitrile)	3.0
poly(vinyl chloride-*g*-methyl methacrylate)	$\simeq 0$
poly(vinyl chloride-*g*-vinyl acetate)	0.5
poly(isobutylene-*g*-styrene)	−1.0

The first and last showed phase separation in the sense discussed above (Fig. 2). The remaining two polymers were of the type represented in Fig. 1. Details of Danon's work are given in Chapter IV, Section 4-B.

It can be seen that for the first case the graft and block copolymers behave like random copolymers, but for the second case there are no common solvents. This situation occurs, for example, for poly(ethylene) grafted with acrylonitrile (Chapiro, 36); for poly(acrylamide-*g*-acrylonitrile)(Henglein, 37); for poly(acrylic acid-*g*-vinyl acetate)(Hart and de Pauw, 38); for poly(ethyl acrylate-*g*-vinylpyridine)(van Paesschen, 39); and for poly(vinyl benzoate-*g*-methyl methacrylate)(Smets, 43). Exceptions were reported by Nowakovski (44) for poly(methyl methacrylate-*g*-acrylic acid) and with some reservations for complicated mixed graft product containing ethylene oxide (Pluronics, 45).

Thus the theoretical treatment given so far has severe limitations, and one cannot escape the feeling that these are due to the intrinsic failure of the statistical approach on which the theory is based. Maron (46) developed functional relations based on the effective volume occupied by a polymer chain that fundamentally seems more appropriate. So far, however, theory dealing with graft copolymers has not been published.

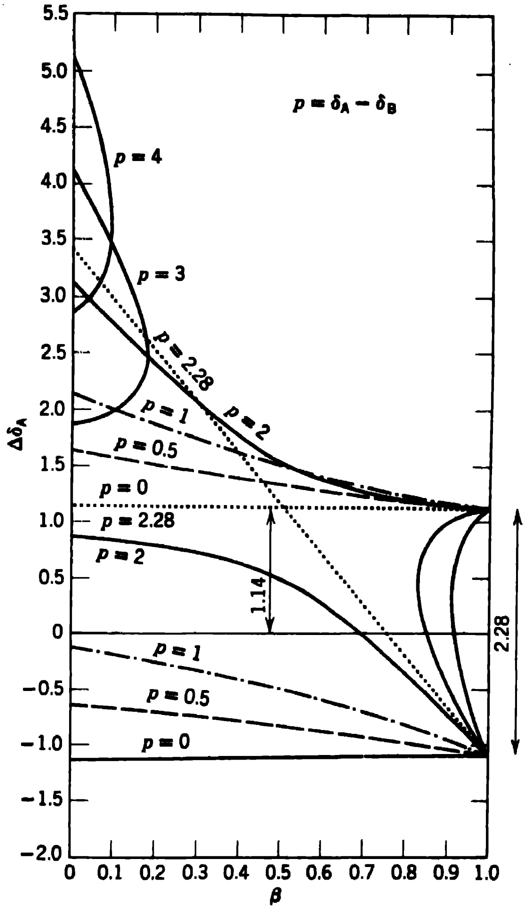


Fig. 2. Phase relationship in graft copolymer solutions (11).
Case 2: $|\delta_A - \delta_B| \gg 0$.

The nonadditivity of solubility characteristics has further been shown by Russian authors (Kargin, Kozlov, and Iovleva, 48–52) and is generally attributed to a decrease in the heat and entropy of mixing and interaction due to grafting. Kargin (53) concluded from his work on mechanochemical grafting that the apparent heterogeneous structure of some graft copolymer–homopolymer mixtures could influence the dissolution of the polymers considerably, and induce false observations on solubility. Chapiro (54) reexamined his results on poly(ethylene-*g*-acrylonitrile) and concluded that the apparent increase in solubility of swelling in xylene at 50°C could be explained by a decrease of crystallinity of the poly(ethylene). Thus, at these temperatures, the decrease of solubility due to grafting could be masked. He finds subsequently, however, that notwithstanding the polarity of the acrylonitrile group, the general rules are obeyed at temperatures above 100°C.

Allen and Gee (55,56) studied the miscibility of polymers in a mutual solvent to derive the polymer interaction constants used earlier, but found that the Flory-Huggins theory broke down and the immiscibility found was less than predicted, and the heat of mixing larger. This is in line with Slonimskii's (47) results based on direct measurement of the heat of mixing of a polymer and solvent, and a pair of polymers and a mutual solvent. Lautout (57) attempted to overcome one of the main failures of the theory. It has been assumed so far, that partition of the solvent between the chains took place proratio of the volume fractions.

Lautout, by using computer techniques, constructed the appropriate phase diagrams and found a deviation with theory. When tested against Danon's experiments a good agreement was found. This study was carried further by Lautout (58,59) with a recalculation of the entropy factor

$$\Delta S = (R/n)(\ln N - 0.32) \tag{17}$$

where n is the average number of chain segments per chain, R the gas constant, and N, the number of configurations of the chain in solution. The effect of configuration on entropy can be seen from the table below for $N = 100$.

Case	Chain Type	ΔS
1	Homopolymer soluble	1.65
2	Copolymer $(AB)_n$, A soluble, B soluble; A and B cannot be first neighbors	1.33
3	Copolymer $(AB)_n$, A soluble, B insoluble; A and B cannot be first neighbors	0.69
4	Copolymer A_nB_n, A soluble, B soluble; A and B cannot be first neighbors	1.50
5	Copolymer A_nB_n, A soluble, B soluble, A and B cannot be second neighbors	1.47
6	Copolymer A_nB_n, A soluble, B insoluble; A and B cannot be first neighbors	0.81
7	Copolymer A_nB_n, A soluble, B insoluble; A and B cannot be second neighbors	0.66

The decrease in entropy compared to case 1 explains anomalous phase separation or a decrease of solubility, as obtained from the Flory-Huggins theory. Kargin (48,53) and his co-workers used a similar concept, but did not give a quantitative evaluation. An attempt to improve the evaluation of the heat term expressed by solubility parameters, using Guggenheim's method, did not lead to an improvement of the earlier equations derived by Lautout (58). The solubility behavior described forms the basis for characterization techniques and will also be used when dealing with the structure of graft copolymers in the solid state.

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2. CONFIGURATION AND STRUCTURE OF GRAFT COPOLYMERS IN SOLUTION*

We have seen that the solubility of graft copolymers, and consequently their solutions, cannot be treated by a single theory, nor described as a simple phenomenon. While in the case of a random copolymer solution behavior can be handled as if it were a new polymer composed of simple monomer units, graft copolymers contain elements of the properties of the composing homopolymer chains. As soon as the interaction between two dissimilar polymer chains becomes predominant, incompatibility, phase separation, configurational effects, become the rule rather than the exception. This was possibly first stated in a digestible form in 1947 by Dobry and Boyer (1). The phenomenon of polymer incompatibility was realized much earlier than this, well before Staudinger (2) recognized high molecular weight chain molecules. This incompatibility between the composing homopolymer chains of block and graft copolymers is the predominant feature not encountered in simple homopolymer or random copolymers. The systems dealing with graft copolymers are also distinguished by a much larger number of degrees of freedom. A homopolymer has already a very large, if not infinite, number of degrees of freedom. By grafting, this number is multiplied considerably by the possible variations in chemical composition, number, position, length, and structure of grafted chains, as well as inter- and intrachain configurational effects.

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* References for this subsection will be found on pages 139–141.

For linear homopolymers one can state the molecular composition simply in the form of molecular weight averages and distributions, only mildly complicated by branching effects and end groups for industrially prepared counterparts. These parameters are accessible through classical physicochemical techniques (for example, 3–5).

Random copolymers can also be characterized by the same methods, to which must be added techniques for the determination of sequential distribution, theoretically (see, for example, 6,7) or experimentally (8).

If, however, one prepares graft copolymers, a mixture usually results consisting of the desired graft copolymer and both homopolymers. As already discussed, the components of this mixture are more often than not difficult to extract due to the complicated solubility behavior. The structure and chemical composition of the graft copolymer can vary considerably without even taking count of its molecular weight (9–11). Consequently, conventional fractionation techniques, if the graft copolymer is soluble at all, become much more difficult and uncertain (12–14). Due to the incompatibility, preferential interaction will occur in solution, resulting in structure formation (Benoit, 15). This structure will occur depending on the concentration on molecular scale for extremely dilute solutions (Benoit, 15) or on macroscopic scale for concentrated solutions (Sadron, 16) extrapolating to structure in the solid state.

A. Structure in Dilute Solution

The best way to describe the behavior of graft copolymers is possibly by means of the accumulated data on styrene–methyl methacrylate blocks and grafts, which have been chosen by many authors as a convenient system since both homopolymers have been extensively studied.

O'Driscoll (17) attempted the copolymerization of styrene and methyl methacrylate with lithium and obtained a block copolymer. He established that acetonitrile is a selective solvent for poly(methyl methacrylate), and will dissolve random copolymers with more than 10% styrene. Extraction with this solvent was followed by extraction of the acetonitrile insoluble fraction with cyclohexane. This solvent is selective for poly(styrene), but will not dissolve random copolymers of styrene and methyl methacrylate. O'Driscoll demonstrated the efficiency of the extraction system on homopolymer mixes. This technique has been used by many other authors. On the basis of solution and bulk physical properties it was concluded that the polymer consisted of alternating blocks of poly(methyl methacrylate) and poly(styrene). The evidence given, however, on solubility and incompatibility in the solid state is relatively poor. O'Driscoll et al. at this stage still accept intrinsic viscosity as a molecular weight measure, notwithstanding that Woodward and Smets (19) showed earlier that poly(styrene-*b*-methyl methacrylate) had a lower intrinsic viscosity than the corresponding homopolymers in the same solvent at the same molecular weight. Sonja Krause (20) produced some very carefully executed work on intrinsic viscosities, radii of gyration, and second virial coefficients of fractions of poly(styrene-*b*-methyl methacrylate) and compared these data with literature values for the random copolymer and homopolymers. In solvents which can dissolve only one of the corresponding homopolymers (acetone and triethylbenzene) the dilute solution properties of the block copolymer indicate micelle formation. This was concluded from visible turbidity as well as an abnormally high molecular weight, compared to those obtained in butanone and toluene solutions. These solvents are common solvents for both components of the chain. In these latter solvents the intrinsic viscosities, radii of gyration, and second virial coefficients of the block fractions were appreciably lower than would be expected from averaging the properties of the equivalent homopolymers. This behavior is opposite to that found for random copolymer fractions by Stockmayer et al. (21) whose intrinsic viscosities, radii of gyration, and second virial coefficients are higher than the average properties of the homopolymer. The butanone data also indicate that the conformation of the block molecules in solution is different from that of the homopolymer or random copolymer molecules. Present data are not sufficient to indicate the exact conformation of these block copolymer molecules.

Burnett et al. (22) extended the investigation over a larger range of compositions. The osmotic pressures in toluene and the viscosities in toluene and methyl ethyl ketone were measured for four homogeneous fractions of poly(styrene-*b*-methyl methacrylate) containing 50–74% styrene by weight. These data were combined with those for poly(styrene) (23–25) and poly(methyl methacrylate) (26).

The entropy of dilution, heat of dilution, and "ideal" temperature parameters all have maxima around the middle of the composition scale. A cancellation effect makes the osmotic second virial coefficient and Huggins' μ almost independent of composition. The results indicate a considerable repulsion between the chemically different halves of a block copolymer molecule.

The molecular extension ratios $(\alpha^5 - \alpha^3)/M$ and unperturbed displacement lengths $(r_0^2/M)^{1/2}$ for the copolymer molecules change very sharply between 50 and 70% styrene. It is suggested that an *intramolecular phase separation* may occur in this composition range. (See Fig. 3.)

Some criticism can be leveled at the work so far presented; the main criticism is concerned with the actual composition and homogeneity of the block copolymer molecules. This was reflected in the work of Urwin and Stearne (27,28) who prepared some poly(styrene-*b*-methyl methacrylate) samples by the living polymer technique, thus achieving relatively sharp molecular weight distributions.

Urwin's molecules consisted of a poly(styrene) block flanked at either side by a poly(methyl methacrylate) block. His data established beyond reasonable doubt that intramolecular interaction is larger than intermolecular interaction for the homopolymer blend. Also, depending on the solvent, phase separation on intramolecular scale, followed by aggregation, must be accepted.

The argument for graft copolymers is complicated by the heterogeneity of the samples presented by various authors (32–40). The radiochemical route to poly(styrene-*g*-methyl methacrylate) was indicated by Ballantine et al. (41) and Hayden and Roberts (42). Poly(methyl methacrylate-*g*-styrene) can be prepared equally well (43–45) as can poly(styrene-*g*-methyl methacrylate) (43,46,47). Mita (30,31) closely followed by Gallot et al. (29) studied the dilute solution behavior of both these graft copolymers. Mita's work on poly(methyl methacrylate-*g*-styrene) does not allow any significant conclusion since the samples were polydispersed in respect to molecular weight and composition. Gallot's samples may not have been

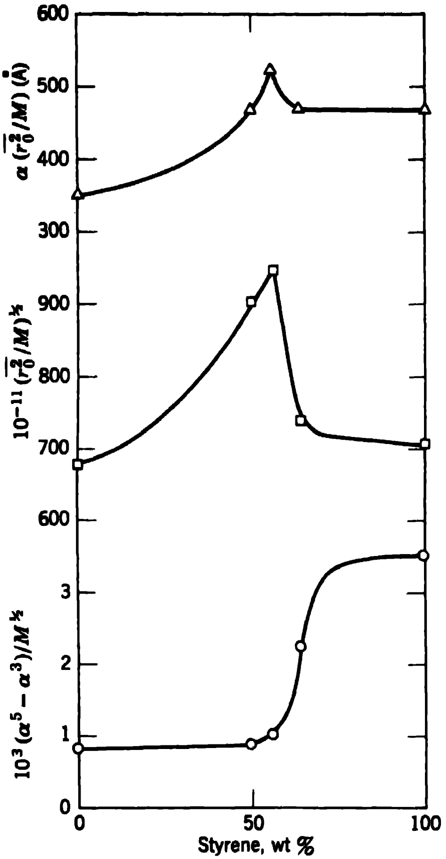


Fig. 3. Configurational parameters as a function of composition for block copolymers in toluene (22).

much better, but his results show differences which cannot be attributed to polydispersity.

In this case the intrinsic viscosity was measured in the system dioxane–cyclohexane as a function of the composition. Dioxane is a good solvent for poly(styrene) and poly(methyl methacrylate); cyclohexane is a nonsolvent (precipitant) for the latter but at 34°C a θ solvent for poly(styrene). The results are represented in Fig. 4.

The intrinsic viscosity decreases in all cases until the point of precipitation. The graft copolymer behaved completely differently from the other

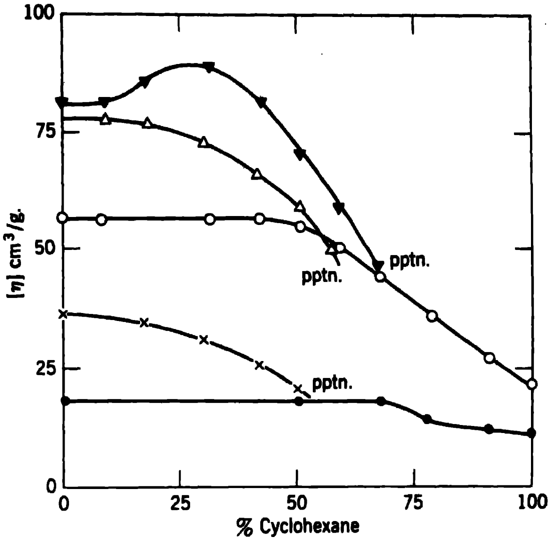


Fig. 4. Intrinsic viscosity in THF solution as a function of added cyclohexane for graft and homopolymers (52).

● Poly(styrene) homopolymer; $\bar{M}_w$ 30,500
× Poly(methyl methacrylate) homopolymer; $\bar{M}_w$ 98,000
▼ Poly(methyl methacrylate-*co*-styrene); 46% PMMA of $\bar{M}_w$ 112,700; 54% PS of $\bar{M}_w$ 132,300; $\bar{M}_w$ 235,000
△ Poly(methyl methacrylate-*b*-styrene); 41% PMMA of $\bar{M}_w$ 180,400; 59% PS of $\bar{M}_w$ 259,600; $\bar{M}_w$ 440,000
○ Poly(methyl methacrylate-*g*-styrene); 11.4% PMMA of $\bar{M}_w$ 98,000; 18 styrene graft chains, each $\bar{M}_w$ 30,500; Total 88.6% PS of $\bar{M}_w$ 540,000; $\bar{M}_w$ 638,000

copolymers and homopolymers. The ratio between the initial and final intrinsic viscosity was as follows:

Polymer	$\frac{[\eta]_{\text{initial}}}{[\eta]_{\text{at pptn}}}$
Poly(styrene)	1.28
Poly(methyl methacrylate)	1.89
Poly(methyl methacrylate-*g*-styrene)	3.0
Poly(methyl methacrylate-*co*-styrene)	1.35
Poly(methyl methacrylate-*b*-styrene)	1.24

The graft copolymer does not behave as an "average" of the homopolymers. This can be explained by internal phase separation. Each molecule becomes a small gel kept in solution by the poly(styrene) chains. Precipitation (e.g., aggregation) did not occur until 98% cyclohexane! This was confirmed by light scattering measurement of the molecular weight. The apparent molecular weight at 0% cyclohexane was 660,000 and at 98% cyclohexane 650,000. This is again confirmed by the radius of gyration which reduced from 280 Å to 160 Å. The hypothesis earlier demonstrated for block copolymers was thus confirmed for graft copolymers.

Climie and White (48) carried out similar experiments for poly(acrylonitrile-*b*-methyl methacrylate) beyond the precipitation point. Except for a perturbing time effect in the aggregation, it was postulated that the preferential interaction between similar chains carried on beyond the precipitation point.

Schlick and Levy (49) investigated structural effects by synthesizing a number of poly(styrene-*b*-isoprene) polymers with identical molecular weight and composition, but varying the sequence length. They found that the precipitation (phase separation) threshold was independent of the length of the sequences, but the intrinsic viscosity increased with decreasing length of the sequences.

Bresler and collaborators (50) confirmed the idea of intramolecular precipitation in dilute solution for poly(styrene-*b*-isoprene), and suggested that the globulization can be extrapolated to concentrated solutions and the solid state.

Tsvetkov (51) noted that poly(methyl methacrylate-*g*-styrene) has positive optical anisotropy, despite the fact that poly(styrene) (making up 90% of the graft copolymer) has negative anisotropy, and postulated that in graft copolymers the chain movement is hindered by the presence of the noncompatible chain. Unfortunately, very little further work has appeared on flow birefringence of graft copolymers and it remains to remember that this hindered movement (or increased stiffness) of the chain must be reflected in effects influenced by anisotropy.

The situation for dilute solutions can be summarized as follows:

1. Solutions in Good Solvent for Both Types of Chains

It has been shown that molecular parameters such as radii of gyration or intrinsic viscosities are not additive properties. This applies also to thermodynamic quantities such as interaction constants and second virial coefficients. It has become clear that the chain configuration is mainly influenced by preferential interaction between like elements. In general the chains of graft copolymers are therefore more compact in solution. Depending on the relation between the interaction constants for chains A and

B with solvent and between the chains themselves, one of the components of the grafts may be more or less extended compared to the other.

2. Solutions in a Solvent Which is a Poor Solvent for One of the Component Chains

If a precipitant for one of the component chains of the graft copolymer is added to solutions, polymer–polymer interaction will take charge and by intramolecular precipitation a microgel particle will be formed. Normally aggregation would follow, but in the case of graft copolymers the soluble chains remaining may form a protective "colloid" thus keeping the particle in "solution." This effect is particularly strong for graft copolymers, but less pronounced for block copolymers. In the latter case plurimolecular gels (52) may be formed, which will be dealt with in the next section.

B. Structure in Concentrated Solutions

Sadron (16) and his collaborators, in pursuit of new media for insertion polymerizations, such as intracanular polymers formed in urea and thiourea complexes (53–57) and clays (58,59), described a new class of substances called "organized polymers." His studies were aimed at the formation of polymers from monomers contained in a space of molecular dimensions and structure, but the data assembled on the structure of concentrated block and graft copolymers are unique in the literature on this subject. Historically many authors noted the first stage of organization in fractionation work, where solutions occurred with high turbidities (see, for example, Refs. 20,50,17,35,52). In nearly every paper dealing with fractionation a note is made of micellor solutions (see fractionation). Merrett (60,61) describes the behavior of micellor solutions of natural rubber-*g*-poly(methyl methacrylate) in detail.

Finaz (62) observed the similarity in behavior of poly(styrene-*b*-oxyethylene) to emulsifiers or soaps in aqueous solutions. This gave Sadron (16) cause to extend the idea of a "molecular micelle" occurring in dilute solutions of graft and block copolymers, consisting of a gel particle of precipitated polymer solubilized by the soluble part of the molecule. (See Fig. 5.) The globular part B, in Fig. 5, does not necessarily have to be in a random configuration, but could take up more regular pattern such as a helix (63,64). In more concentrated solutions multimolecular micelles occur, as demonstrated by a large increase in molecular weight (Finaz, 62). In the more concentrated solutions, structures can be formed analogous to those occurring in concentrated soap solutions (65–68); thus the terminology used in the latter case can be transferred without change.

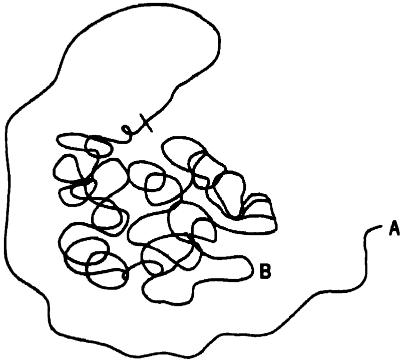


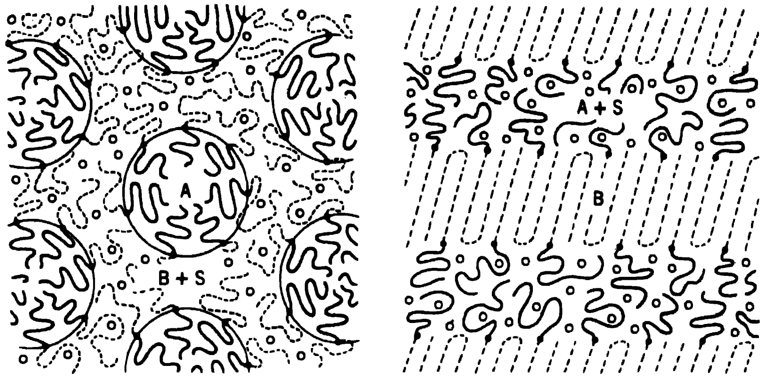
Fig. 5. Model of a "molecular micelle."

When molecular micelles of graft and block copolymers, with constituent chains of largely different solubility characteristics, agglomerate to form gels with ordered configurations over distances that are long compared with the molecule, one could say that these gels were mesomorphic and amphipolar. With suitable choice of the components A and B, the solvent S, and the concentration, the liquid crystals encountered in soap solutions can be reproduced by solutions of block and graft copolymer.

Mesomorphic gels can occur in two structures: leaflike (smectic, 69) or cylindrical (nematic). Skoulios (70,71) identified these structures for the system poly(styrene-*b*-ethylene glycol)–butyl phthalate or nitromethane. The structure identified is schematically given in Fig. 6. Sadron and his collaborators confirmed these structures for the following combinations of a poly(styrene-*b*-oxyethylene glycol) containing 41% styrene with

methyl methacrylate	smectic
isoprene	smectic
vinyl acetate	smectic
acrylonitrile	smectic
poly(ethylene oxide)	smectic
acrylic acid	nematic

The observations were confirmed for the system poly(styrene-*b*-oxyethylene glycol)–ethylbenzene by Gallot (52) without, however, a structure analysis. Skoulios (72) has also described the behavior of poly[styrene-*b*-(oxyethylene-*co*-oxypropylene)] adding one more structure, wherein the precipitated chains are organized in ribbons rather than cylinders or layers.



(a) (b)

Fig. 6. Structure of mesomorphic gels (76): (a) cylindrical structure; (b) leaflet structure. A, poly(styrene) block (full lines); B, poly(oxyethylene) (broken lines); C, solvent (circles).

Gallot also reports that the structures so far discussed with block copolymers as examples apply equally to grafts without, however, giving details.

Ren (74) investigated concentrated solutions and gels of poly(vinyl alcohol-*g*-vinyl acetate) and poly(vinyl-alcohol-*g*-methylacrylate). Sirakashi (75) treated concentrated solutions and gels as a swollen network. Hughes and Brown (73) investigated the solution behavior of poly(ethylacrylate-*g*-styrene) reporting structures and phase separation for concentrated solutions without elucidating the detailed microorganization of the gels formed.

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3. COMPATIBILITY AND STRUCTURE IN THE SOLID STATE*

For the relatively short time graft copolymers have been studied, little attention has been paid to the properties and structure of the solid state. There is still no theory (1,2) available which allows the prediction of bulk properties, and the concept that these properties are determined by one or the other partner of the graft has not maintained its validity. The constituent monomers are not the sole determining factor and the plurality of possibilities of combination has so far defied the establishment of simple rules.

It must be remembered that most polymers, either as polyblends or grafts, are not compatible (3–5). Consequently, some rate phenomena influencing the bulk properties as a function of temperature and time history must be expected.

Specific structures are observed in graft copolymer solutions at high concentrations (see Sect. IV,2,B) and it was suggested that these structures might extrapolate to the bulk polymer. It appears logical, therefore, to see first of all, how the properties of graft copolymers are related to those of the component homopolymers in the two extreme cases.

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* References for this subsection will be found on pages 147–149.

1. The constituent homopolymers are completely incompatible and different in character.

2. The constituent homopolymers are very similar and compatible.

A. Incompatible Homopolymers

Kargin (2) recently described some significant experiments in the first category. He evaluated the properties of starch-*g*-poly(styrene) (6), starch-*g*-poly(methyl methacrylate) (7), poly(vinyl alcohol-*g*-styrene) (8), and poly(acrylic acid-*g*-styrene) (8). The first two were prepared by ozonolysis of starch and the latter two by mechanochemical methods. The properties of these grafts were evaluated by a thermomechanical method (9) wherein the deformation of a solid sample under a given load (penetrometer type) was measured as a function of temperature. Plots for various compositions of the starch-*g*-poly(styrene) showed that the glass transition of most samples was close to that for poly(styrene) of a similar molecular weight, but will only show elasticity and no fluidity even at a starch content as low as 15%. An analogous behavior was found for starch-*g*-poly(methyl methacrylate), the elastic region being rather wider; poly(vinyl alcohol-*g*-styrene) behaved similarly.

The three types of graft copolymers, with components differing sharply in their properties, are composed of hydrocarbon and water-soluble chains. This means that the components are completely incompatible (insoluble in each other) and the homogeneity of the system is maintained only by chemical bonds between the two types of chain.

The postulate of microseparation as demonstrated in solution is not difficult to maintain in solid systems (for example, Hughes 10,11), and the apparent retention of the component properties is mainly due to this process.

Kargin (12) subsequently investigated the limits of this additivity by dilution with a plasticizer for one or the other of the components, such as tetraline and glycerine for poly(vinyl alcohol-*g*-styrene). The glass transitions of either the styrene or vinyl alcohol chains change with plasticizer content as if the opposing component is not present.

It is characteristic of this type of graft copolymer that addition of only one type of plasticizer converts them into a viscous fluid. Thus for poly(vinyl alcohol-*g*-styrene) (48), the addition of 35% tetraline fails to give marked fluidity, but 25% glycerol turns the polymer into a viscous liquid. Simultaneous addition of glycerine and tetraline moves both glass transitions independently, and the addition of 20% tetraline and 25% glycerol turns the polymer into a liquid at 40°C.

The above simple experiments would tend to show that the continuous phase consists of poly(vinyl alcohol). Merrett (13,14) observed that rubber-*g*-poly(methyl methacrylate) can exist in two forms, having the properties of rubber and poly(methyl methacrylate), respectively, depending on the formation from solution favoring one or the other component. This superficial evidence for the existence of a continuous and discontinuous precipitated phase, still remains to be clarified by more stringent methods. It is a pity that no evidence has been offered for bulk polymers as was provided by Sadron and his collaborators (see Chapter IV, Section 2-B) for concentrated solutions. The polymers do not need to be chemically dissimilar to show phase separation or other characteristic behavior of the systems under study. A good example is the system poly([iso] styrene-*g*-[a] styrene) studied by Kargin and collaborators (15,16). This system shows all the characteristics of a heterogeneous graft copolymer, if the original crystallinity is not destroyed by solution. On dissolving and reprecipitation, the system acted like a branched styrene. Annealing partially restored the heterogeneous characteristics. Kargin confirmed the structure by x-ray analyses and electron microscopy.

Kargin (17) again postulates globular and fibril structures in amorphous polymers offering distinct interfaces. If such structures are formed by coiled molecules of similar composition in graft copolymers, analyses by electron microscopy should be possible, after treatment with appropriate solvents. This was shown for poly(oxypelargonate-*g*-acrylic acid) (18).

In general, graft copolymers of two crystalline constituents will retard or inhibit crystallization and lead to globular or fibril formation but not crystallinity. This was observed by Merrill (19) for poly(bisphenol-*b*-oxyethylene glycol).

The structure of graft copolymers formed from crystalline base material is complicated by inhomogeneous grafting at interfaces. A good demonstration of these effects can be found in the structural analyses of poly(tetrafluoroethylene-*g*-styrene) by Jendrychowska-Bonamour (20). Two types of heterogeneity could be detected, one of which could be observed with a microscope. Similar data were obtained by Chapiro (21,22) for poly(ethylene-g-acrylonitrile). In all cases crystallinity of the base polymer gave rise to inhomogeneous grafting at the interface; on subsequent destruction of this structure and crystallinity, recrystallization was retarded or inhibited and globular structures resulted.

Beevers (37) examined poly(methyl methacrylate-*b*-acrylonitrile), poly(methyl methacrylate-*co*-acrylonitrile), and poly(acrylonitrile-*g*-methyl methacrylate) by x-ray techniques and could not detect specific structural effects notwithstanding the incompatibility of the polymers.

Skoulios (42) showed x-ray evidence, however, of structure in poly(styrene-*b*-ethylene oxide) using small angle techniques.

Kargin (2) studied systems in which both components were crystalline, e.g., nylon 6-*g*-poly(ethylene oxide). In the graft copolymer only nylon 6 spherulites could be induced, with a melting point reduced proportional to the poly(ethylene oxide) content. In equivalent blends both components crystallize. Again, the averaging of the properties of the partners in the graft did not take place.

Stamm (23) investigated the structure of poly(propylene) figures grafted with chloromethylstyrene, but concluded that any structure shown in electron micrographs of "homogeneously" grafted fibers were voids. The chloromethylstyrene graft chains were probably too short to show structure due to the expected incompatibility, chloromethylstyrene being an excellent chain transfer agent.

Rossi (41) showed organized structures in poly(dimethyl siloxane-*b*-ethylene oxide) and poly(dimethyl siloxane-*b*-propylene oxide) by measurements of internal pressure. The experimental pressures were in excess of calculated values indicating strong organization.

Some structural data are available for poly(butadiene-*g*-styrene-*co*-acrylonitrile) ABS type compounds. The ABS polymers in general can be divided into two classes—polyblends and grafts—and consequently should offer a fruitful field for structural studies. Eden (24), who recently reviewed the physical properties of both classes, demonstrated the superiority in general properties of the graft type. Howard (25) and Staverman (26) have shown the microstructure in ABS-type grafts and rubber reinforced poly(styrene), respectively. These clearly demonstrate inhomogeneity and globular regions of homogeneous components. The effect appeared much the same as the fracture surface of a 24 ST aluminium alloy which contained inclusions of a second phase. The spherical aggregation is similar to that of poly(styrene-*b*-methyl methacrylate) from solution, observed by Newman (27). He postulates aggregation of one component, followed by aggregation of the second component around the first formed globule.

Hughes and Brown (10) made similar observations on films formed from latices, in which two polymers were polymerized in sequence. These authors also noted that it was possible to prepare clear films from two incompatible polymers, such as poly(methyl methacrylate) and poly(styrene). These films showed separation when strained (11).

Goldberg (43) showed x-ray evidence in films of poly(bisphenol-A-*b*-

oxyethylene) of ordered structures due to the bisphenol A blocks. Crystallinity of the poly(oxyethylene) blocks was absent.

Considerable work has been done in recent years on stereoblock copolymers and homopolymers introduced by Natta (28) and his collaborators. Wolf (29,30) discussed physical properties of these polymers, which differ from the corresponding blends, and came to the conclusion that some structure on molecular scale was necessary to explain his results but did not disclose details. This is a rather interesting feature since incompatibility cannot be the cause of the structure in this case.

Pigagniol (31) found that a small amount of a suitable graft copolymer could make a blend of the corresponding homopolymers compatible. Kargin and his school have in an oblique way supported this argument.

It is thus apparent that the absence of phase separation, as judged from the appearance of films of the polymers (be it blend, graft, or block), cannot be taken as a lack of structure on a microscale, or as a sign of compatibility. Hughes (4,10) and O'Driscoll (32), for example, have also shown that apparently clear compatible films of either of the three types of polymers can show irreversible whitening when strained; this was then explained by phase separation. The authors (33,34) have shown that phase separation and structure are a sharp function of composition and can be thermodynamically predicted, but equilibrium conditions in solid polymeric samples may only be reached after long periods. For example, poly(vinyl chloride-*g*-methyl methacrylate), originally a clear, transparent substance without microscopically and visually observable structure, showed phase separation after eight months storage at room temperature, as predicted by Kern (35).

Since incompatibility has been used as the basis for structure in graft copolymers of largely different monomers, a kinetic factor should be added. Some of the observations of previous workers (10,11,32,31) could be influenced by the time to reach equilibrium conditions in the solid state, and apparent inconsistencies thus explained. This observation was confirmed by Slonimskii (36) on blends of various polymers.

From what little evidence we have on structure, the graft copolymer must have a continuous phase in order to form a coherent mass. The nature of the continuous phase can often be deduced from mechanical properties (Merrett, 13,14, for example). This becomes difficult when the components are available in comparable amounts or at the extremes of the composition range. As soon as the concept of "average" properties breaks down, as indicated earlier, the identity of the continuous phase becomes doubtful.

Rembaum (38), for example, found an unusual behavior for poly(2-

vinylnaphthalene-*g*-ethylene oxide). The modulus–temperature curves showed a greater mobility for graft molecules than for the corresponding blend. The specimen of the graft copolymer was opaque at room temperature, indicating incompatibility, but when heated above 65°C (the melting point of poly(ethylene oxide)) became clear, to turn opaque again at 120°C. The "well" observed in the modulus could be explained by a change in continuous phase from poly(ethylene oxide) to poly(2-vinylnaphthalene). It is unfortunate that no other evidence along these lines has been offered so far.

Baccaredda (39) used dynamic mechanical measurements of graft copolymers and blends to elucidate differences in bulk behavior and structure. The utility of his measurements has potential. The author, however, on the basis of his measurements concludes that for poly([butadiene-*co*-acrylonitrile]-*g*-[styrene-*co*-acrylonitrile]) considerable shielding of CN groups occurred in the graft compared to the blend. This could indicate, for example, that the styrene–acrylonitrile side chains do not take part in the continuum and only the CN groups on the base chain remain effective. This observation is significant since Battaerd and Tregear (33) demonstrated that simple thermodynamics, using the Scatchard–Hildebrand equation in regions where it should not apply, could predict phase separation in graft copolymers. If structure in bulk graft copolymers does occur (and it is at least plausible that it does), this structure interferes with normal inter- or intrachain interactions. Supporting evidence was given by Magat (40) on the accessibility of COOH groups in nylon-*g*-poly(acrylic acid) reduced by shielding.

B. Compatible Homopolymers

A branched chain polymer is probably the best example of this class. (Properties of branched polymers have been described elsewhere (44,45).) The borderline between compatibility and incompatibility is rather vague, particularly since, as seen previously, considerable differences can occur in compatibility in blends or grafts due to shielding. According to Tompa (46) and Scott (47), the behavior of ternary systems consisting of two polymeric components in a single solvent is indicative of the behavior of binary blends of the same polymers.

Kern (35) found experimentally that poly(vinyl chloride) was incompatible with poly(methyl methacrylate) in tetrahydrofuran at 15% w/w but compatible under the same conditions with poly(ethyl methacrylate). He used Small's (48) method to calculate solubility parameters for these polymers, and found that the results corresponded with the theory.

When, however, these polymers are grafted on PVC, the poly(vinyl chloride-*g*-methyl methacrylate) is compatible at first appearance, but will show incompatibility under strain or with time (Battaerd and Tregear, 33). A number of such instances were reported also by Hughes and Brown (10,11). According to Bartenev (49), compatibility is indicated by a single second-order transition point for polymer blends. This is, however, in direct contradiction with many other authors who claim that whatever the compatibility of the components of the graft or blend, the individual transition temperature will be maintained. In general, properties will be very much like a blend of the homopolymers. These properties will be discussed in the appropriate section.

Very little, if any, work has been reported on possible structures or absence of structures in this class of polymer.

Tsvetkov (50), investigating the photoelastic effect of poly(methylmethacrylate-*g*-styrene) and poly(butyl methacrylate-*g*-styrene), made some interesting observations throwing light on the coexistence of the component chains. In the glassy state the copolymers remained isotropic. The temperature interval of the viscoelastic state is narrow and the glass transition temperature T_g, is near the flow temperature T_f. Near T_f, a high positive birefringence Δn develops; after stretching the film and after removing the stress Δn slowly relaxes; $\Delta n < 0$ near T_g; between T_g and T_f a negative Δn develops immediately after imposing the stress, but Δn increases with time and changes from − to + because of the increase of a + anisotropy. After removing the stress, the negative Δn vanished at once, whereas the positive Δn decays slowly. The photoelastic properties differ sharply from those of corresponding homopolymers. The P/S side chains have high negative anisotropy and the maximum of its polarizability is parallel to the main chain, so that the whole macromolecule exhibits a + anisotropy. The negative effect is connected with the orientation in the direction of stretching the side chains and has low relaxation times. The + effect, slowly developing and relaxing, is due to the orientation of the main methacrylate chain and of the whole macromolecule.

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4. CHARACTERIZATION OF GRAFT COPOLYMERS*

A. General

The characterization techniques applicable to homopolymers and random copolymers are generally applicable to graft and block copolymers. These techniques are described in a number of textbooks and monographs, some of which are listed in references (1–3,7). These methods, however, need modification due to the intrinsic composition and solution behavior of graft copolymers. Some of the more common modifications will be discussed in the following sections.

For the complete identification of a block or graft copolymer, the following information is required:

1. The overall composition
2. The overall molecular weight
3. The composition of each sequence
4. The average length of each sequence
5. The number of sequences or branches per macromolecule
6. The order of sequences (block copolymers)
7. The classification of each sequence in the case of graft copolymers as backbone or branch

The identification of a block or graft copolymer is further complicated by the presence of varying amounts of homopolymer, depending on the method of formation. Such homopolymer has to be separated before the graft proper can be analyzed. Ceresa (3) reviewed some methods; additional information can be found in his monograph (5) and Burlant and Hoffman's book (6).

B. Fractionation

The more common fractionation techniques have been reviewed by Ceresa (3,5) and Ham (7). For detailed information reference should be made to these texts.

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* References for this subsection will be found on pages 173–176.

It should be kept in mind, however, that whichever way fractionation is carried out (by fractional precipitation or fractional elution) a distinction should be made between component separation, molecular weight separation, or composition separation of the graft. This can be accomplished by the use of selective solvents. Primary separation of homopolymers is achieved by using solvents which will only dissolve one homopolymer but do not affect the other homopolymer nor the graft copolymer. For the system poly(styrene)–poly(styrene-*g*-methyl methacrylate)–poly(methyl methacrylate) the following solvents can be used (8,9): cyclohexane for poly(styrene), acetonitrile for poly(methyl methacrylate). Champetier (10) used dimethylsulfoxide and carbon disulfide for poly(methyl methacrylate) and poly(styrene), respectively.

Micelles of the graft will form in acetone, a nonsolvent for poly(styrene), and triethylbenzene, a nonsolvent for poly(methyl methacrylate) (11). These solvents cannot be used, therefore, to separate the two homopolymers from the graft. Unfortunately, very few clear-cut examples have been published so far.

The selection of suitable solvents for other systems is complicated by the solubility behavior of graft copolymers with largely different components. Chapiro (12) investigated, for example, the solubility behavior of the system poly(styrene)–poly(styrene-*g*-acrylonitrile)–poly(acrylonitrile). Fig. 7 has been abstracted from Chapiro's paper.

It must be noted that in curves 2 and 3 the graft has a higher solubility than the corresponding homopolymers but, at concentrations of 0.08% and higher, the effect tends to reverse. This system therefore does not lend itself to separation of the three main components or fractionation.

Chapiro classed precipitants in three groups for dimethyl formamide solutions.

1.	$\delta_p > \delta_{\mathrm{PAN}}$	The graft is more soluble than poly(acrylonitrile); (water, methanol, propanol).
2.	$\delta_{ps} < \delta_p < \delta_{\mathrm{PAN}}$	The poly(styrene) is more soluble than the graft, which in turn is more soluble than poly (acrylonitrile): (benzene, toluene, dioxane, chloroform).
3.	$\delta_p < \delta_{ps}$	The graft is less soluble than poly(styrene): for example, *n*-hexane, cyclohexane.

The choice of precipitant or solvent–precipitant system is therefore quite critical and more selective than in the case of homopolymers.

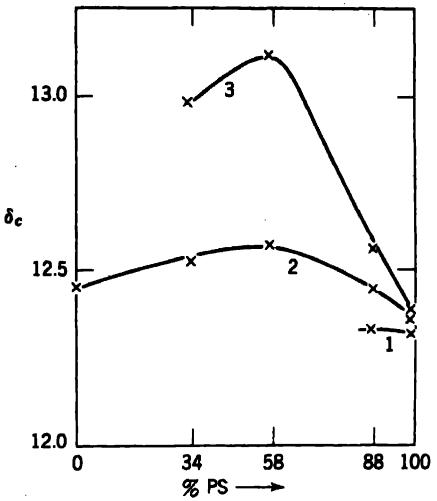

Fig. 7. δ_c, the critical energy density at the point of precipitation, as a function of poly(styrene) content of poly(styrene-*g*-acrylonitrile) in the system dimethylformamide–water. Polymer concentrations of curve 1, 0.4%; curve 2, 0.08%; curve 3; 0.02%.

Similar eccentricities in behavior were described for starch-*g*-poly(styrene) by Kargin (13), poly(styrene-*g*-acrylic acid) by Kozlov (14). A reduced solubility of grafts compared to homopolymers was reported by Kargin (15–17) and his school. Kargin (18) also warned that dissolution could be incomplete and difficult in complicated mixtures, thus predicting the above problems for the field of selective extraction.

Danon (19) studied the systems poly(isobutylene-*g*-styrene), poly (vinyl chloride-*g*-acrylonitrile), poly(vinyl chloride-*g*-methyl methacrylate), poly(vinyl chloride-*g*-vinyl acetate), poly(vinyl chloride-*g*-methyl methacrylate). These polymers were divided into two classes.

(*1*) The Scatchard–Hildebrand solubility parameters δ for the homopolymers are nearly the same as in poly(vinyl chloride-*g*-methyl methacrylate) or poly(isobutylene-*g*-styrene). In this case solubility follows an additive role (see Chapter IV, Section 1–B, *2*) but separation of the three components is difficult.

(*2*) The Scatchard–Hildebrand solubility parameters δ of the homopolymers are very different and the anomalous behavior reported by Chapiro earlier, takes place. Selective extraction may work for selected solvent systems.

A new method, gel permeation chromatography (20), may find application in graft copolymer (21) fractionation, but still has to be proved in practice. This method sorts macromolecules to size, and can be applied only if both homopolymers and the copolymer have a common solvent.

C. The Significance of Intrinsic Viscosity Measurements of Graft Copolymers

The intrinsic viscosity of a simple polymer is related to its average molecular weight, distribution, and statistical size in a given solvent system. Experimentally it is easily determined. The intrinsic viscosity can be defined by the following equations (24).

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c \tag{1}$$

$$(\ln \eta_r)/c = [\eta] + k''[\eta]^2c \tag{2}$$

where

$$[\eta] = \left(\frac{\eta_{sp}}{c}\right)_{c\to 0} \equiv [(\eta_r - 1)/c]_{c\to 0}$$
$$= [(\ln \eta_r)/c]_{c\to 0}$$

$$k'' = k' - \frac{1}{2} \tag{3}$$

k' and k'' are approximately constant for a given system and temperature, but are structure-sensitive.

Martin (25,26) introduced the relation

$$\log\left(\frac{\eta - \eta_0}{\eta_0 c}\right) = \log[\eta] + \frac{k'[\eta]c}{2.303} \tag{4}$$

which holds to a higher concentration. Because of its better fit, the Martin equation should be used if any significance has to be given to variations of k' with structure. For graft copolymers, therefore, the Martin plot is preferred.

The intrinsic viscosity is usually related to relevant molecular parameters by the following equations (Mark, 22; Houwink, 23)

$$[\eta] = K\overline{M}_v^a \tag{5}$$

$$\overline{M}_v = \left[\frac{\Sigma_i M_i^{a+1/2}N_i}{\Sigma_i M_i N_i}\right]^{1/a}$$

K and a are constants dependent on the solvent–solute system, and $\bar{M}_v$ is the viscosity average molecular weight. For extended, strictly rodlike solute molecules, the exponent a should have the value 2. For the other extreme, solute molecules so tightly coiled that they can be considered as spherical with no draining of solvent molecules through them, a should be zero and the intrinsic viscosity independent of molecular weight. For molecules that are kinked in a purely random way, the exponent should have a value somewhat less than unity.

Any molecular interactions that increase or decrease the average degree of extension of the solute chain molecules should correspondingly increase or decrease the exponent a. Consequently, in graft copolymers, a may be used as a measure for grafting provided an accurate estimate of the molecular weight is available.

According to Flory, the intrinsic viscosity is related to molecular parameters as follows:

$$[\eta] = \Phi(\bar{r}_0^2/M)^{3/2}M^{1/2}\alpha^3 \tag{6}$$

Φ = Flory universal constant 3.62×10^{21}
M = molecular weight
α = expansion factor
$\bar{r}_0^2$ = root mean square end to end distance for unperturbed polymer which may be reduced to

$$[\eta] = KM^{1/2}\alpha^3 \tag{7}$$

K = a constant independent of solvent and molecular weight.
K may vary with temperature since $\bar{r}_0^2/M$ will vary with temperature.

In an ideal solvent or θ–solvent

$$[\eta]_\theta = KM^{1/2} \quad \text{and} \quad \alpha = 1 \tag{8}$$

The θ point of a solvent is identified as the temperature at which the second virial coefficient for a poor solvent becomes zero.

The above equations allow a separation of the thermodynamic and molecular weight effects and, furthermore, thermodynamic data can be obtained with

$$\alpha^5 - \alpha^3 = 2C_M\psi_1(1 - \theta/T)M^{1/2} \tag{9}$$

C_M = parameter depending on polymer type only
ψ_1 = parameter characterizing the entropy of dilution

These equations have been applied for many polymers with some success.

The theory supporting the equations has been modified many times (20,29–32) and still has only limited application (33). It is of interest to explore if any of these equations, conventionally applied to solutions of linear homopolymers, can still be used for solutions of graft copolymers.

In the first instance, a graft copolymer is a branched polymer. Manson and Cragg (34) prepared grafts of styrene on poly(styrene). It was expected that k' would have a higher value for the graft copolymer than for the linear polymer. The experimental value, however, did not show this, and was (within experimental error) equal to the value found for the linear polymer dissolved in the same solvent. This is surprising since k' can be used as a measure for branching (Huggins (35) supported by ample experimental data (36,37)). Manson and Cragg suggest that in these data either cross-linking or bushy branches (branched branches) caused the increase in k'. Thus k' may be effective in distinguishing between the two types of branching, single or bushy. It would seem then that what affects k' is not branching per se, but branching of such a type and to such a degree that the segment density in the molecular coil is significantly altered (as would be the case for multiple branching).

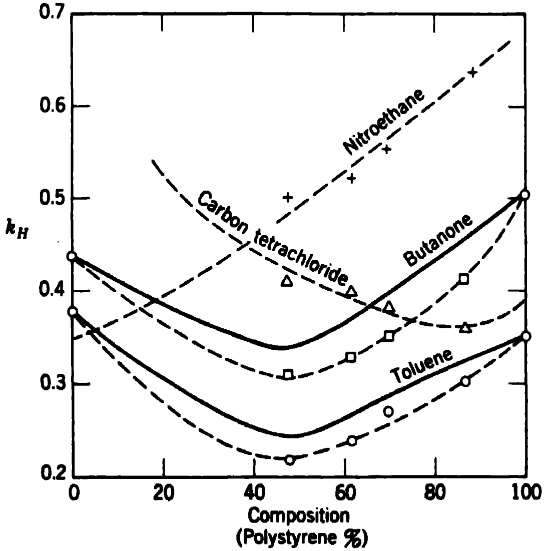

Fig. 8. The viscosity constants (Huggins constant k_H) as a function of polymer composition for poly(styrene-*b*-methyl methacrylate) (39).

The segment density in the molecular coil would be influenced by branches of a different polymer, as occur in a graft copolymer. Urwin and Stearne (38,39) recently investigated the behavior of k' as a function of composition for some carefully prepared block copolymers poly(styrene-*b*-methyl methacrylate) and obtained the curves presented in Fig. 8. The full lines in this figure represented values for k' calculated according to a formula given by Cragg and Bigelow (40) for simple mixtures of molecules.

$$k'_M = \frac{k'_A[\eta]_A^2\omega_A^2 + k'_B[\eta]_B^2\omega_B^2 + 2k'_Ak'_B[\eta]_A[\eta]_B\omega_A\omega_B}{([\eta]_A\omega_A + [\eta]_B\omega_B)^2} \tag{10}$$

k'_A, k'_B	Huggins k' for polymers A, B
$[\eta]_A$, $[\eta]_B$	intrinsic viscosities polymers A, B
ω_A, ω_B	weight fractions of polymers A, B

The deviation between theoretical and experimental lines could, with caution, be interpreted as the repulsion between unlike polymer components in the graft copolymer being larger than in a simple mixture. Both butanone and toluene are good solvents for both partners in the block, poly(styrene) and poly(methyl methacrylate). When a solvent was chosen which was specific for either constituent, such as carbon tetrachloride or nitroethane, considerable deviation from the additive rule occurred.

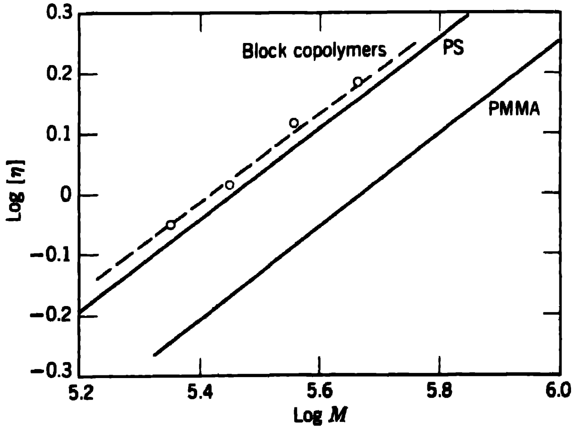

Fig. 9. Log $[\eta]$ versus log M for block copolymers in toluene (39).

This deviation from simple additivity was encountered in previous sections for the case of graft copolymers with constituents without mutual solvents. It can be seen from the above that k' for graft copolymers may be affected by composition and solubility factors, and should not be used without supporting evidence, as evidence for grafting. Urwin and Stearne also explored the use of the Mark-Houwink equation (eq. 5, p. 152; Fig. 9). The intrinsic viscosity appears to be higher than for either of the homopolymer constituents of the same molecular weight. This interpretation, however, is only tentative. Burnett et al. (41) reported similar findings earlier for the same type of polymers.

The empirical relations 1–5, therefore, can be used provided the interpretation is treated with caution until many more data are available. Krigbaum and Wall (42) proposed the equation

$$\eta_{sp,m} = [\eta_1]c_1 + [\eta_2]c_2 + b_{11}c_1^2 + b_{22}c_2^2 + 2b_{12}c_1c_2 \quad (11)$$

$\eta_{sp,m}$ = specific viscosity of mixed polymer solution
$[\eta_1]$ $[\eta_2]$ = intrinsic viscosities components 1, 2
c_1c_2 = concentrations of components 1, 2
b_{11}, b_{22} = intraspecific interaction parameters of components with solvent only
b_{12} = interspecific interaction parameter

b_{12} can be expressed as (42)

$$b_{12} = (b_{11}\,b_{22})^{1/2}$$

or as

$$b_{12} = (b_{11} + b_{22})/2,$$

as postulated by Catsiff and Hewett (43).

It was found that b_{12} was sensitive to the averaged surface presented by a polymer in a particular solvent. Thus for poly(methyl methacrylate-*g*-lauryl methacrylate)b_{12} is sensitive to temperature due to the uncoiling of the hydrocarbon side chain in nonpolar solvents, and consequent failure of the proposed equation. Although the equations used by Catsiff and Hewett may still need testing, they show promise in the determination of configuration.

Various attempts have been made to use eqs. 6 to 9 in one form or another. The characteristic use of these equations is coupled to the determination of the θ temperature.

These temperatures are usually obtained for homopolymers from:

1. Osmotic and light scattering measurements over a range of temperatures in a poor solvent. θ may be identified as the temperature at which the second virial coefficient is zero.

2. Determination of the consolute temperature for a number of fractions followed by extrapolation to infinite molecular weight.

3. Determination of the critical point in a ternary system as a function of temperature or solvent nonsolvent composition for infinite molecular weight.

It is obvious that a θ temperature does not exist for a graft copolymer, but θ temperatures may be known or experimentally accessible for the component chains.

Methods *2* and *3* for the determination of θ call for homopolymer fractions having homogeneous molecular weights. In graft copolymers homogeneity in all respects of composition and structure should be added to this condition. Strict application of theory therefore becomes prohibitively difficult.

A number of authors have drawn conclusions from "apparent" values obtained in conditions where the equations are not applicable. Discussion of the utility of such calculations is therefore necessary.

Burnett et al. (41), for example, derived thermodynamic parameters this way for poly(styrene-*b*-methyl methacrylate). Data derived for this system were given in Fig. 3, Chapter IV, Section 2. Apparent θ temperatures were derived from osmotic and light scattering measurements and the authors accepted the constancy of Φ, the universal constant for the system.

Krause (11), for the same type of polymer, deduces values of Φ using "apparent" molecular weights obtained from light scattering data. Φ so calculated is far from constant and varied from 0.14×10^{21} to 2.46×10^{21} and Krause concludes that equations of the form of 7 cannot be applied. The anomalous behavior of the intrinsic viscosity of poly(methyl methacrylate-*g*-styrene) in a solution of a precipitant for the backbone (a solvent for poly(styrene)) was illustrated earlier in Fig. 4. Gallot (44) attempted a quantitative interpretation of these data for poly(methyl methacrylate-*g*-styrene) in a solution of a precipitant for the backbone, but a solvent for poly(styrene). A star with *n* equal branches was used as a model for this situation giving

$$\bar{S}^2 = 3\bar{S}_A{}^2$$

where $\bar{S}^2$ is radius of gyration (average square) of the graft and $\bar{S}_A{}^2$ is the equivalent for the branch chain for long branches and a very large number of branches.

For small numbers

$$\bar{S}^2 = \bar{S}_A^2(3 - 2/n)$$

n being the number of branches.

Theoretical and experimental values are still an order of 2 different (86 Å and 160 Å, respectively). Bresler (45) confirmed that for poly-4, 5(styrene-*b*-isoprene) when one of the blocks is "precipitated," the usual intrinsic viscosity–size relations gave inaccurate results for good solvents for both components. Flory's equation holds within the experimental accuracy.

A number of authors reported the failure of quantitative relationships of the intrinsic viscosity equations; Chinai et al. (46, 47) for poly(isopropylstyrene-*g*-methyl methacrylate), Dondos (48) for poly[(3,3-diphenyl-1-propene)-*g*-styrene], Korshak et al. (49) for poly(ethylene terephthalate-*g*-methyl methacrylate), and Gurgenidze (50,51) for poly[*N*-(6-carboxylhexyl)methacrylamide-*co*-styrene)-*g*-ω-hydroxyenanthic acid]. The latter author, however, found a semiquantitative relation between Huggins' k' and regularity of chain branching.

Kawai (52) reported the effect of shear rate in an attempt to quantitatively interpret intrinsic viscosities of poly(styrene-*g*-acrylonitrile) in benzene methanol mixtures.

The validity of eqs. 6–9 for graft systems requires more evidence than is presently available and results can be accepted on a tentative basis only.

D. The Significance of Light Scattering Techniques in the Graft Copolymer Field

The application of light scattering techniques to graft copolymers involves difficulties similar to those encountered in intrinsic viscosity studies. A closer examination of methods based on colligative properties of polymer solutions, where a single numerical result coupled to a known concentration allows the calculation of an average molecular weight, shows that the results should always be applicable to copolymers. In other words, it should always be possible to obtain a number average molecular weight whatever the fluctuations in the polymeric composition.

If the system is monodisperse in composition, no difficulties should be encountered either in light scattering or sedimentation, since there is little to distinguish the copolymer from the homopolymer. If, however, polydispersity occurs in composition, both the specific refractive increment dn/dc and partial specific volumes will depend on composition.

Another complication can be expected when the graft copolymer has no common good solvent for the composing chains and the backbone, or the grafted chains are in a "precipitated" form. The use of solvent mixtures may involve preferential adsorption by the components.

For the purpose of the present treatment, the virial expansion of the equation of state relating to Rayleigh scattering from a solution of a heterogeneous (in molecular weight) solute can be written as

$$\frac{Kc}{R(\Theta)} = \frac{1}{\sum_i M_i P_i(\theta) W_i} + 2A_2c + 3A_3c^2 + \dots \tag{1}$$

where

$$A_2 = M_w^{-2} \sum \sum B_{ij} M_i M_j W_i W_j$$

$$K = 2\pi^2 n^2 \left(\frac{dn}{dc}\right)^2 \Big/ N\lambda^4$$

The symbols have the following significance:

M_i	molecular weight of polymer species i, comprising a weight fraction W_i of the solute
c	total polymer concentration in units of mass per unit solution volume
$R(\theta)$	excess scattering at an angle θ from the direction of the incident beam
$P_i(\theta)$	intensity distribution normalized to unity for $\theta = 0$ for an isolated molecule of species i
$A_2 A_3$	second, third virial coefficients by approximation (more exact for small and for molecules small compared to the wavelength)
N	Avogadro number
λ	wavelength of incident light *in vacuo*
n	refractive index of solution *in vacuo* for light of incident wavelength λ
(dn/dc)	refractive index increment with concentration assuming that all species have the same increment

This equation is applied in practice by extrapolation to obtain $(Kc/R(\theta))_{c=0,\theta=0}$ as described by Zimm (54) and by other appropriate procedures (see, for example, 55). In this procedure dn/dc, the refractive index increment, and $P(\theta)$, the particle scattering factor, will be influenced by heterogeneity in composition as well as solubility effects.

Stockmayer and co-workers (56) derived for random copolymers the following relation

$$\left(\frac{I(\theta)}{K'c}\right)_{c=0,\theta=0} = \left(\frac{dn}{dc}\right)_0^2 \overline{M}_w + 2b\left(\frac{dn}{dc}\right)_0 + \langle M\Delta X\rangle + b^2 \langle M(\Delta X)^2\rangle \qquad (2)$$

$I(\theta)$ = ratio of the intensity of scattered light measured at angle θ and at a fixed distance from the scattering volume to the intensity of light incident on the solution

c = concentration of polymer solution

$(dn/dc)_0$ = measured refractive index increment of the copolymer–solvent system

K' = $2\pi^2 n_0^2 K/\lambda_0^4 N$

n_0 = refractive index of the solvent for light of wavelength λ_0 *in vacuo,*

N = Avogadro's number

K = function of θ, which includes the instrumental calibration constant

b = $(dn/dc)_{\mathrm{A}} - (dn/dc)_{\mathrm{B}}$

where A and B refer to the parent homopolymers. The scattering is dependent upon the composition distribution of the copolymer by the relations

$$\langle M\Delta X\rangle = \sum W_i M_i (\Delta X)_i$$
$$\langle M(\Delta X)^2\rangle = \sum W_i M_i (\Delta X)_i^2$$

where W_i is the weight fraction of the molecules in the sample with molecular weight M_i and composition X_i with $(\Delta X)_i = (X_i - X_0)$ and X_0 the composition of the sample.

An apparent value of the molecular weight is, therefore, found for block and graft copolymers, after extrapolation to zero scattering angle and to infinite dilution.

The equation proposed by Stockmayer contains three unknowns: $\overline{M}_w$, $\langle M(\Delta X)\rangle$, and $\langle M(\Delta X)^2\rangle$. These quantities could be obtained by measurements of light scattering and $(dn/dc)_0$ in three different solvents.

Krause (57) checked the Stockmayer equation for poly(styrene-*b*-methyl methacrylate) in six solvents and found that the equation was adequate. Similarly, Bushuk and Benoit (58,59) found that the Stockmayer equation qualitatively described the light scattering behavior of a number of styrene–methacrylate copolymers. Urwin (38,39) carried out a light scattering study of poly(styrene-*b*-methyl methacrylate) of homogeneous composition and consequently confirmed the extrapolation for $(\Delta X)_i = 0$ and $(\Delta X)^2 = 0$. It would therefore appear that the Stockmayer theory is adequate and also yields two parameters $\langle M(\Delta X)\rangle$ and $\langle M(\Delta X)^2\rangle$ describing the composition distribution.

Krause (57,11) proposed the following two equations relating the apparent and true molecular weight averages and radii of gyration, based on the Stockmayer theory

$$\left(\frac{dn}{dc}\right)_0^2 M_{\mathrm{app}} = \left(\frac{dn}{dc}\right)_0^2 \overline{M}_w + 2b\left(\frac{dn}{dc}\right)_0 \langle M(\Delta X)\rangle + b^2 \langle M(\Delta X)^2\rangle \tag{3}$$

$$\left(\frac{dn}{dc}\right)_0^2 M_{\mathrm{app}}\, (\overline{S}^2)_{\mathrm{app}} = \left(\frac{dn}{dc}\right)_0^2 \langle M_w(\overline{S}^2)\rangle + 2b\left(\frac{dn}{dc}\right)_0 \langle M(\Delta X)(\overline{S}^2)\rangle + b^2\langle M(\Delta X)^2(\overline{S}^2)\rangle \tag{4}$$

Leng and Benoit (60) derived a similar equation in a slightly different form. The discussion so far presupposed that the copolymers could be obtained in solution, that a good solvent was available for both components simultaneously, and that for a full evaluation at least three such solvents could be found. It was previously noted that these conditions would be difficult to realize. As a matter of fact, the difficulty in characterization of graft copolymers is caused by an anomalous solubility behavior. The Stockmayer equation, primarily derived for random copolymers, where solubility is not an overriding factor, does not cover the more common case for grafts and blocks, where the solvent usually is only a "good" solvent for one of the component chains. Krause (57) having derived the following quantities for unfractionated poly(styrene-*b*-methyl methacrylate)

$$\overline{M}_w = 1.22 \times 10^6, \quad \langle M\Delta X\rangle/\overline{M}_w = -0.16, \quad \text{and} \quad \langle M(\Delta X)^2\rangle/\overline{M}_w = 0.15$$

from data in six different solvents finds that in acetone, a bad solvent for poly(styrene), that the ratio $M_{\mathrm{app}}/\overline{M}_w$ is as high as 400. Values for $(\overline{S}^2)$ and the second virial coefficient were also found to be excessive (11).

The ratio $M_{\mathrm{app}}/\overline{M}_w$ in good solvents is of the order of 2. This can be explained by micelle formation containing approximately 100 molecules per micelle. From the radii of gyration it was possible to show that the micelles contained very little solvent. This explanation, however, does not eliminate the fact that if acetone had been used as one of the solvents in the original measurements, Stockmayer's equation would have failed.

Benoit (62) proposed a relation of the form

$$M_{app} = M_w + 2Py + Qy^2 \tag{5}$$

where P and Q are parameters characteristic of the polydispersity of the sample and

$$y = \frac{(dn/dc)_A - (dx/dc)_B}{(dn/dc)_0} \tag{6}$$

Calculations for a simple two-block copolymer were carried out by Benoit (62). Leng (63) worked out expressions for more complicated cases. Benoit's concept is shown in Fig. 10 specifying the various quantities which permit the determination of the parabola expressed by eq. 5. Mita (64) carried out these calculations for poly(methyl methacrylate-*g*-styrene) (Fig. 11). Benoit (62) similarly obtained Fig. 12 for poly(styrene-*b*-methyl methacrylate). The derivation of radii of gyration from light scattering data, appears simple at first glance. In the case of a block copolymer one would expect the length of the chain to be equal to the sum of the length of the individual blocks. This simple rule has many exceptions. Schlick and Levy (65) prepared poly(styrene-*b*-isoprene) copolymers of a fixed molecular weight but varying in number and molecular weights of the individual blocks. The intrinsic viscosity was not constant but varied

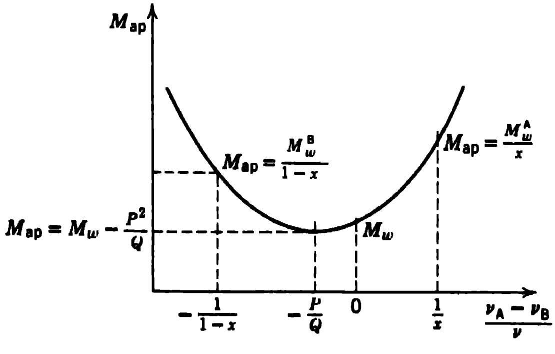

Fig. 10. The different quantities which permit the determination of the molecular weight parabola.

with the number of blocks indicating an interaction between dependent elements. The use of the intrinsic viscosity for the determination of radii of gyration was dealt with in Chapter IV, Section 2. Benoit and co-workers (67) derived the following equation for the relation between the apparent

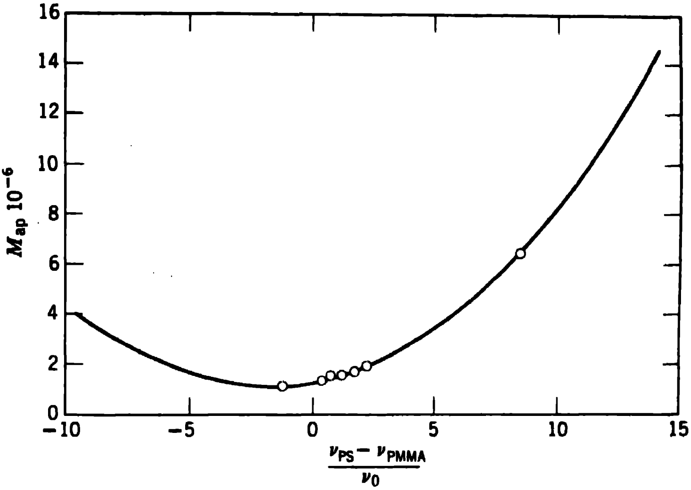

Fig. 11. Variation of the apparent molecular weight of poly(methyl methacrylate-*g*-styrene) as a function of the refractive index increment ratio (64).

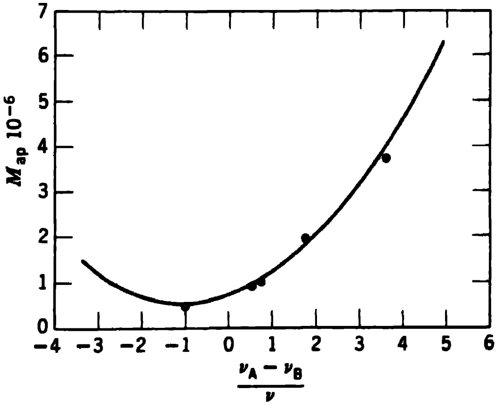

Fig. 12. Variation of the apparent molecular weight of poly(styrene-*b*-methyl methacrylate) as a function of the refractive index increment ratio (62).

radius of gyration R_{app} and the radii of gyration R_A and R_B of the constituent chains of the copolymer

$$R_{app}^2 = \left(X\frac{\nu_A}{\nu_0}\right)R_A^2 + \left[(1 - X)\frac{\nu_A}{\nu_0}\right]R_B^2 + X(1 - X)\frac{\nu_A\nu_B}{\nu_0^2}L^2 \tag{7}$$

where X is the fractional composition of the polymer. ν_A ν_B and ν_0 correspond to $(dn/dc)_A(dn/dc)_B$ and $(dn/dc)_0$ used earlier and L is the distance between the centers of gravity of component chains A and B. This formula shows that the measured R_{app} only gives a relation between R_A^2 R_B^2 and L^2, while the true radius of gyration is given by

$$R^2 = XR_A^2 + (1 - X)R_B^2 + X(1 - X)\,L^2 \tag{8}$$

Since ν_A and ν_B can be negative, negative radii of gyration can be obtained as shown by Leng (67) and co-workers.

Leng and Benoit (61) made a very interesting study of the light scattering of copolymers of the type B–A–B in a solvent with a refractive index equal to the homopolymer B. They measured the radius of gyration R_A^2 and observed the effect of the presence of B.

Thus for poly(styrene-*b*-methyl methacrylate) in the form PMMA–PS–PMMA, they obtained Fig. 13 holding the poly(styrene) chain at a constant molecular weight, but varying the molecular weight of the poly(methyl methacrylate) chains. With an increase in the methacrylate content, an increased volume effect is shown by the radius of gyration of the poly(styrene) chain (Leng and Benoit, 68).

The application of light scattering measurements on graft copolymers is still problematic and can only be carried out for copolymers which have a

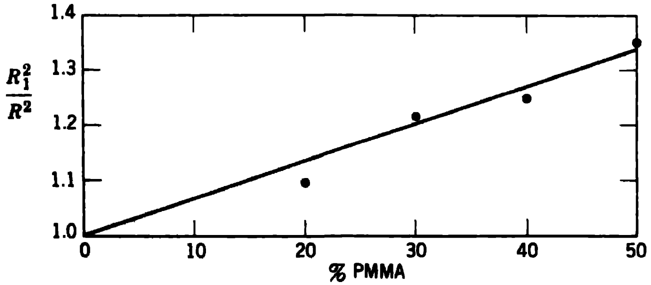

Fig. 13. Variation in the radius of gyration of the poly(styrene) chains in the block copolymer sequence (PMMA-PS-PMMA) as a function of percentage poly(methyl methacrylate) (62).

common good solvent for component chains. Derivative data should be treated with reserve, particularly when molecular weights of component chains and the composition distribution are unknown. However, some recent publications have added to the store of data. Holahan (114) gave some very carefully analyzed data for poly(*p*-isopropylstyrene-*g*-ethyl methacrylate). Separation, grafting, and characterization were evaluated by the use of labeled compounds (as indicated by Kaemmerer (117)), IR, and NMR. Polowinski (116) similarly gave data based on I^{131} labeled poly(methyl methacrylate) graft chains in poly(vinyl acetate-*g*-methyl methacrylate).

Dondos (115) extended previous work already quoted, and determined molecular configuration in binary solvents for poly(diphenyl-3,3-propene-1-*g*-styrene) and poly(diphenyl-3,3-propene-1-*g*-methyl methacrylate). These last three investigations confirm the pattern so far set and show that the generalizations made are likely to be valid.

E. Ultracentrifugation

Density gradient centrifugation is one of the more recent techniques applied to copolymers. The literature consequently is still limited and very few examples are available. Earlier, Shashoua (69) and co-workers separated graft copolymers made from microgel from mixtures using sedimentation velocity techniques. Density gradient centrifugation, pioneered by Meselson, Stahl, and Vinograd (70) mainly applied to biological systems, but owing to the theoretical work of Hermans (71,72), it can be used for the determination of composition distributions in copolymers. Hermans and Ende (73) recently reviewed the field thoroughly.

Ende and Stannett (74) applied the theories of Hermans (75,76) to the system cellulose acetate-*g*-poly(styrene). The density gradient was formed from bromoform–dimethyl formamide systems. The initial sample showed two peaks. They were found to be pure graft copolymer and poly(styrene); the latter was easily removed by extraction with benzene. The composition of the graft copolymer was determined from the buoyant densities of the graft and the two homopolymers and found to be 49% styrene, 51% cellulose acetate, compared with 44.1 and 55.9%, respectively, estimated from the weight loss after acid hydrolysis.

The discrepancy between the two methods may be attributed to two or three effects still neglected in present theory. Benoit (62) stated these effects in the following terms:

1. The effect of diffusion may be of considerable consequence for small peaks at the limit of resolution. Erroneous results may be obtained if the sample is very heterogeneous.

2. With the attainable speeds of rotation and available organic solvents (severely limited by the solubility of the polymer), only limited density differentials can be obtained. Consequently, when the homopolymers differ largely in density a number of runs may have to be done to obtain a complete picture, each one of which is already a time-consuming experiment.

3. A number of authors have indicated that results may be in doubt because of preferential absorption, at least of the binary solvent mixture. The density gradient is caused by a concentration gradient. The preferential absorption may well be a function of the position of the polymer fraction in the gradient, but will also be a function of the composition of the polymer. Bresler (77,78), Benoit, and Buchdahl et al. (80) have dealt with this effect in a quantitative manner.

Unfortunately, both theory and experimental work are still in the formative stages. Detailed description of methods and theory, therefore, will be omitted here.

Baranovskaya (108) made a detailed study of the sedimentation properties of poly(methyl methacrylate-*g*-styrene) and poly(butyl methacrylate-*g*-styrene), differing in graft distribution and the molecular weights of side and main chains. He concluded that the sedimentation diffusion analysis of graft copolymer structure is possible.

Bresler (109) used a density gradient technique on poly(methacrylate-*g*-isoprene). Corrections for selective solvation by one of the components of the solvent mixture were applied, based on blank experiments with the homopolymers. Experiments were carried out at higher than normal concentrations leading to a possible determination of the partial specific volume of the graft copolymer.

F. The Significance of Osmometry of Graft Copolymers

The osmotic pressure of graft copolymer solutions like other colligative properties, has to be approached with caution, when interpretations based on contemporary solution theories are used. The osmotic pressure observed for a well-fractionated sample with a reasonably high molecular weight (thus independent of the membrane) can be used to calculate the molecular weight.

The osmotic pressure in dilute solution can be represented by any one of the following three forms:

$$\frac{\pi}{c} = \frac{RT}{M} + Bc + Cc^2 + \ldots \tag{1}$$

$$\frac{\pi}{c} = RT\left(\frac{1}{M} + A_2c + A_3c^2 + \ldots\right) \tag{2}$$

$$\frac{\pi}{c} = \left(\frac{\pi}{c}\right)_0 (1 + \Gamma_2c + \Gamma_3c^2 + \ldots) \tag{3}$$

where the constants B, C, A_2, A_3, Γ_2 Γ_3, are all referred to as the virial coefficients.

The number average molecular weight is usually obtained by plotting π/cRT as a function of the concentration, followed by extrapolation to zero concentration. A number of extrapolation methods have been proposed (2-4).

The power series expressed by eqs. 1, 2, and 3 indicate that, depending on the validity of the theory involved, a true molecular weight should result, independent of the relations between the virial coefficients and molecular parameters. Osmotic measurements should give a "true" number average molecular weight if a graft copolymer can be obtained in solution without the formation of aggregates or "micelles" as discussed in Chapter IV, Section 2-B.

The basic power series for osmotic pressure can, at high dilution, be written in the form

$$\frac{\pi}{c} = \frac{RT}{M}[1 + \Gamma_2c + g\Gamma_2^2c^2] \tag{4}$$

since powers greater than c^2 can generally be ignored at high dilution. This equation, in general, yields a curved graph for π/cRT versus c, since the cubic term only becomes negligible for small Γ_2. This curvature may complicate extrapolation procedures. It has been noted (2,3) that at the Θ temperature the shape and curvature terms in eq. 4 are zero, thus considerably simplifying extrapolation procedures. The Θ temperature of graft copolymers is, however, of doubtful value and does not apply in most cases, except for very similar backbone and graft chains.

Alternatively, a more flexible procedure is to work with the polymer dissolved in a mixture of solvent and nonsolvent. Additions of nonsolvent bring the system close to the precipitation point and the slope of the reduced osmotic pressure curve becomes negligible (Gee, 81; Scott, 82;

Mark, 83). At equilibrium in this method, the composition of the solvent is not the same on either side of the membrane; as a consequence the time required for equilibrium may be prolonged.

In most graft copolymers, a single solvent is not likely to be a good or a bad solvent for both component chains. The slope will be affected to some extent since one of the chains will be in most cases close to "precipitation." The procedure of Gee, Scott, and Mark may not be applicable but a reduced curvature should be expected.

Burnett et al. (41) and Urwin and Stearne (38,39) provide the only two detailed investigations on the osmotic pressure of graft and block copolymers. Both are concerned with poly(styrene-*b*-methyl methacrylate). Neither of these authors report consistent results on slopes or curvature.

The factor g in eq. 4 generally has a value of 1/4, although $g = 5/8$ is the theoretical upper limit for noninterpenetration spheres (84).

Equation 4 can be written in the form

$$(\pi/cRT)^{1/2} = M^{-1/2}[1 + 1/2\ \Gamma_2 c] \tag{5}$$

for $g = 1/4$. Thus plotting $(\pi/cRT)^{1/2}$ against c should give a straight line of intercept $M^{-1/2}$ and slope $^1/_2\ \Gamma_2 M^{-1/2}$.

Burnett reports curves convex toward the c axis for such plots for experimental data for block copolymer fractions, but Urwin claims rectilinear plots for similar data. Similarly Burnett prefers $g = 5/8$, while Urwin in turn finds $g = 1/4$ adequate. The same discrepancy occurs when comparing the values for Γ_2 for these authors.

Burnett (41) attempted to evaluate Γ_2 in terms of dilute solution thermodynamics together with the intrinsic viscosity. The value of this approach was discussed in Chapter IV, 2-A.

Osmometry can be used to obtain a number average molecular weight of a graft copolymer under the proviso that the solutions do not show aggregation or micelle formation. The derivation of thermodynamic parameters from osmotic measurements has not yet been demonstrated satisfactorily.

G. Miscellaneous Characterization Techniques

A number of characterization techniques, other than the classical examples discussed so far, have been used in isolated instances. The results show considerable potential and therefore should be included in this review.

1. *Flow Birefringence*

Experience has shown that anisotropy of a monomer unit within a chain is a sensitive index of its structure and can therefore be made use of in the elucidation of this structure.

Some general rules have been established (2) which give a qualitative guidance in the interpretation of results.

1. Carbon to carbon-type polymer molecules without bulky side groups, usually demonstrate a positive anisotropy: cyclic structures in the chain increase this effect. Si—O and Si—C bonds are very weakly anistropic.

2. Increasing the length of side groups decreases the positive chain anisotropy, and may cause a change in sign or an increase in the negative anisotropy. Rings with conjugated double bonds strongly affect negative anisotropy.

3. The negative anisotropy of the chain which results from the presence of side groups depends on the flexibility of the side group.

4. Isomerization and deformation of valency angles also have an effect on the anisotropy.

Tsvetkov (85,86,106) and his school measured the flow birefringence of poly (methyl methacrylate-*g*-styrene) and Mitsengendler (87) of poly-(butyl methacrylate-*g*-styrene). In this case the optical anisotropy of grafted side chain is negative, i.e., the maximum polarizability is in the direction normal to the side chain and parallel to the basic chain. Thus, the graft polymer has a high positive anisotropy despite the fact that the basic chain by itself barely demonstrates any optical anisotropy and the poly-(styrene) chains constitute nine-tenths of the mass of the graft polymer and are negatively anisotropic.

Tsvetkov's results are summarized in the table below. The enormous positive value of $\alpha_1 - \alpha_2$ observed in the case of the graft polymers indicates that these chains are more rigid than the corresponding chains of the

Segmental Anisotropy $\alpha_1 - \alpha_2$ of Poly(methyl Methacrylate-*g*-Styrene)

M_w main chain	M_w graft chain	Av. no. of graft chains/ molecule	No. of graft chains/100 monomer units of main chain	Wt % of grafted styrene in polymer	M_w graft copolymer	$(\alpha_1 - \alpha_2) \times 10^{25}$ cm^3
7×10^4	2×10^3	315	45	90	7×10^5	+ 870
58×10^4	2×10^3	1850	32	86	41.5×10^5	+ 750
58×10^4	10×10^3	420	7	88	48×10^5	+7000

constituent homopolymers. Therefore, this technique, could yield useful data on structure, but has only been used in this isolated instance.

Tsvetkov (107) also investigated the photoelastic effect as a characterization tool.

2. *X-ray Scattering in Graft Copolymers*

Beevers (89) compared the physical properties of poly(methyl methacrylate-*b*-acrylonitrile) with poly(methyl methacrylate-*co*-acrylonitrile). His results indicated that, collectively, differences in x-ray scattering from these polymers should be observed. Beevers (88) subsequently made a detailed investigation of powdered samples, including poly(methyl methacrylate), poly(acrylonitrile), and poly(acrylonitrile-*g*-methyl methacrylate). His results are best represented by his summary in Fig. 14. The inter-

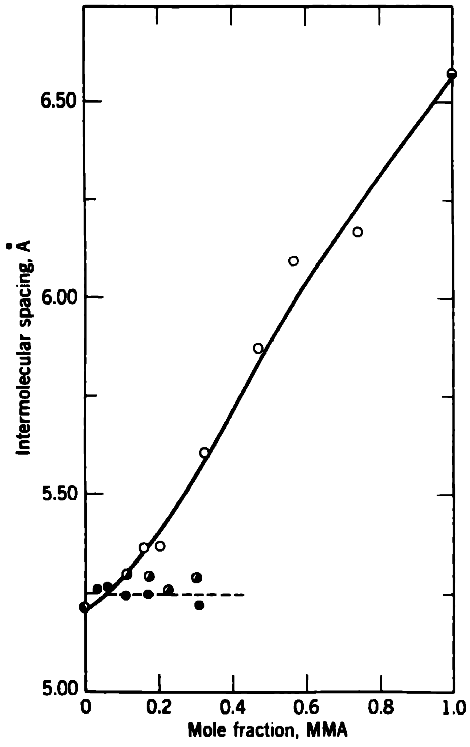

Fig. 14. Effect of copolymer composition on the intermolecular spacing in block, random, and graft methyl methacrylate and acrylonitrile copolymers (88).
●, Block: ○, random; ◐, graft; ◑, PAN; ◑, PMMA.

molecular spacing does not seem to vary for the block and graft copolymers and the random copolymer showed a progressive change in pattern from poly(acrylonitrile) to that of poly(methyl methacrylate) with a change in copolymer composition. The molecular packing of poly(acrylonitrile) is apparently only slightly affected by the graft or block chain.

A similar effect was noted by Coleman (90) for poly(ethylene terephthalate-*b*-oxyethylene glycol). Hachihama et al. (91) examined poly-(ethyl acrylate-*g*-acrylonitrile) with similar results; however, in this case the spacing was sensitive to heat treatment and drawing.

Sella (92) investigated the structures and morphologies of poly(ethylene-*g*-styrene), poly(ethylene-*g*-vinyl acetate), poly(ethylene-*g*- vinyl toluene), poly(ethylene-*g*-acrylonitrile), and poly(ethylene-*g*-methyl methacrylate) with large and small angle techniques. It was found that, in general, the grafting reactions (initially preirradiation with gamma rays) were heterogeneous, leading to the coexistence of three phases, mainly nongrafted poly(ethylene), grafted copolymer, and homopolymer.

Ho (113) evaluated the structure of poly(propylene-*g*-acrylonitrile) where the base fiber used for grafting was oriented suggesting the molecular structure of the graft. He also compared this structure with an oriented fiber made from poly(propylene-*g*-acrylonitrile).

X-ray techniques, however, have not proven to be of general usefulness. The cases quoted here all contain a crystalline and noncrystalline component and no data are available for two crystalline components or two totally amorphous components, where applications become more restricted.

3. Polymer Monolayers

Monomolecular films or monolayers of polymers have been used to elucidate structural features (2). Techniques and results up to 1957 have been reviewed by Crisp (93). One or two selected papers will be discussed here to emphasize the potentialities of the study of monolayers in the characterization of graft copolymers.

It may be concluded from general data that mixtures of (polar) polymers give a surface pressure-area isotherm close to the calculated average curve (for poly(vinyl acetate)–poly(vinyl benzoate), see (94)). The pressure at collapse may, however, deviate from the average, depending on packing (see, for example, poly(vinyl acetate)–stearic acid (95)).

Distinction can be made between the homopolymers, singly and mixed, and a random copolymer. Hammond and co-workers (96) applied some of the principles found by Ries, Beredjick, and Gabor (94,97) to graft copolymers poly(isobutene-*g*-methyl acrylate) as a function of the number and molecular weight of the branch chains.

Poly(isobutene) does not spread at the air–water interface. The graft copolymer containing 50% w/w of each component, with 2 to 3 branches per molecule does, however, spread. From the isotherm the limiting area for the monomer units could be calculated. The presence of the branches prevented the collapse of the isobutene chain which, according to the figures presented by Hammond, should be present in an extended state, contrary to the nonspreading (collapsed) homopolymer.

The study by Beredjick (98,99) of poly(methyl methacrylate) in its various forms of tacticity showed that surface pressure-area isotherms and derivative data can be used to distinguish isotactic, atactic, syndiotactic, and stereoblock poly(methyl methacrylates) and mixtures thereof from the stereoblocks. This tool has not as yet been used to any extent in the characterization of graft copolymers.

4. Infrared Spectroscopy

Infrared spectroscopy has been infrequently used. The value of such spectra is consequently still in doubt. Graft copolymers of the heterogeneous type, with grafted chains of comparable length with the backbone, show IR spectra which, for the strong bands, seem to be additive for the backbone and side chain.

The authors (100) used IR spectra as an analytical tool to determine the content of grafted material (after solvent extraction) for PVC grafted with a variety of vinyl monomers. The IR spectra of the graft copolymers were compared with synthetic "blends" of known composition for calibration, but no significant difference could be detected between the spectra of grafts and blends.

This opinion, however, is opposed by a number of authors who claim to prove grafting by IR spectra. Ohshika (101), for example, used this method to prove grafting for chlorinated isotactic poly(propylene) and vinyl monomers. Marupov (102) similarly claims proof of grafting of poly(2-methyl-5-vinyl)pyridine to cellulose by IR spectra.

In general, however, the authors' view (100) is supported and IR spectra of grafts are taken to be a superposition of the spectra of the corresponding homopolymers. Amamiya (103) used spectra to prove that the grafted product of poly(ethylene) with propylene and SO_2 had a 1:1 composition in the grafted chain by comparison with the isolated copolymer. Araki (104) analyzed poly(ethylene terephthalate) grafted with styrene, acrylic acid, and (2-methyl-5-vinyl)pyridine in a similar fashion. Greber (105) used IR to analyze the tacticity of the grafted chains of poly[(styrene-*co*-butadiene)-*g*-propylene] prepared by heterogeneous catalyses.

The examples quoted are by no means exhaustive, but serve to prove the principle of additivity.

5. Gas Chromatography

The pyrolysis of graft copolymers, followed by gas chromatography of the pyrolytic products, has been recently published. Gaczynski (110) described an application to natural-*cis*-1;4-poly(isoprene-*g*-methyl methacrylate) and natural-*cis*-4;1-poly(isoprene-*g*-styrene). Jobst (112) similarly described the analysis of poly(ethylene-*g*-styrene). Kysel (111) established that blends of poly(propylene) and poly (styrene) give the same result as the corresponding poly(propylene-*g*-styrene). Blends can therefore be used for calibration, provided the number of grafting points is small enough not to affect the amount of poly(styrene) given off. Tacticity of the backbone has no effect.

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5. THE BULK PROPERTIES OF GRAFT COPOLYMERS*

A. Introduction

The commercial importance of any polymer is ultimately determined by its physical and processing properties, i.e., the mechanical properties of the solid and the rheology of the melt. A large number of publications have been reviewed dealing with methods of formation of grafts and the equally voluminous patent literature will be discussed in Part II of this book. The literature dealing with bulk properties, however, is very restricted and, as will be shown in the following pages, these properties are not fully understood. Furthermore no coherent theory has been developed to allow the test of a systematic approach against experimental results.

Notwithstanding the fact that some optimistic reviewers (1,2) are inclined to treat graft copolymers as a panacea for tailor-made polymers, others (3) bluntly state that grafts behave as the blend of the corresponding homopolymers and therefore have little practical importance. It is a fact, however, that very few grafts have reached the market (Chapter V) a fact which may initially be attributed to the intractability of properties. The difficulty in characterization, and consequently in production control, also have contributed to the slow acceptance of graft copolymers. The two existing monographs devote very little space to physical or melt properties. Ceresa (4), for example, discusses in detail only natural rubber-*g*-poly(methyl methacrylate) marketed as Hevea Plus and some types of poly(butadiene-*g*-styrene); Burlant and Hoffman (5) similarly do not treat bulk properties to any extent. It is therefore opportune to look for reasons why graft copolymers have been so slow to develop commercially. Some of these are obvious from previous sections.

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* References for this subsection will be found on pages 224–232.

First, the likelihood of structure has been pointed out and sensitivity to history must be expected to have a larger effect for grafts than for homopolymers. This is particularly true for those grafts which contain incompatible elements. Merrett (8) has shown, for example, that natural rubber-*g*-poly(methyl methacrylate) can exist in two states with totally different properties. Since most grafts have incompatibility built in, this behavior may be quite general. A simple graft copolymer, consisting of a backbone chain and one or more graft chains of a length comparable to the backbone, will behave in the first approximation as a blend on the two corresponding homopolymers, only restricted in the extent to which movement and separation of the two types of chains can occur.

Polymers in general are not compatible, a fact which can be derived from simple qualitative thermodynamic considerations (6). Tompa (7) found that a binary system of two polymers of comparable molecular weight behaves normally except for the functionality of the interaction constant for the polymers, the intensity of which is inversely proportional to the number of segments. At the critical point this interaction becomes very small, and so only a minute positive first-neighbor interaction free-energy will produce incompatibility. Two high polymers are mutually compatible with each other only if their free energy of interaction is favorable, i.e., negative. Since the mixing of a pair of polymers, like the mixing of simple liquids, in the great majority of cases is endothermic, incompatibility of chemically dissimilar polymers is observed to be the rule and compatibility the exception. A graft copolymer in general will have chains which are chemically linked but incompatible and the physical state of this situation is still somewhat of a conundrum.

There are two broad classifications of copolymer types:

1. Copolymers which exist in two or more phases in bulk.

2. Copolymers which do not show phase separation.

Thus the first class contains all nonuniform copolymers, particularly block and graft copolymers, but also random copolymers with a considerable deviation from true randomness. In heterogeneous nonrandom copolymers, the polymer usually consists of sequences of one constituent chain precipitated as droplets in a matrix of the other constituent. If, however, the blocks or grafts are extremely short, the phase separation may not occur. The size of the precipitated droplets will depend upon the length of the blocks and grafts, as well as upon the interaction energy between the chemical constituents. Such a two-phase system will show physical properties analogous to mechanical mixtures of two different polymers. Each phase will show its normal, or near normal, glass temperature. For this reason, one cannot speak of the glass temperature for a block or graft copolymer, for it will often show evidence of two glass transitions or a broad transition region.

In the first instance, therefore, graft copolymers of the heterogeneous type would behave as "polyblends." Tobolsky (11) states categorically that graft and block copolymers are just another way of achieving a successful polyblend, with only one restriction: polymer constituents of the blends and the corresponding copolymers must be amorphous and remain amorphous when strained. Under these conditions he claims that the rule of corresponding temperatures will apply to polyblends as well as graft copolymers. Nielsen (9) states a similar opinion. Graft copolymers are similar to polyblends in their dynamic behavior. Two damping peaks occur unless the constituent chains are mutually compatible, and the only major change in properties can be expected by "phase reversal," i.e., the continuous matrix is formed either by the backbone or the grafted chain (Stein, 10).

Based on these general observations there is little, if any, encouragement to produce grafts and blocks to achieve "novel" physical properties. A closer investigation, however, shows that not all literature data available compare with these general statements, and unexpected effects can be achieved. This is largely due to the fact that, while a large number of graft copolymers have been produced, characterization and examination of physical properties have not kept pace with synthesis.

B. Melt Properties

In Chapter IV, Sections 2 and 3 the plausibility of structure formation in solution and in the solid state, due to the incompatibility of the components of graft and block copolymers, was pointed out. The assumption could therefore be made that the melt rheology of these polymers might throw some light on this structure. Again this subject does not figure prominently in the literature and some confusion seems to exist as to the cause of flow anomalies, particularly when the grafts are formed by a radiation method (Takamatsu, 12). Absence of flow is often attributed to crosslinking, rather than structure formation, but many authors (13–19) neglect the matter of structure or phase separation to a large extent. It is useful, therefore, while reviewing existing data, to examine the facts presented on the assumption that, with very few exceptions, all solid graft copolymers will have either the backbone or the grafted chains in a collapsed form precipitated in a continuum of the other component, and that possibly some preferential interaction will exist between like components resulting in a macrostructure.

In subsequent sections it will be pointed out that graft copolymers have two glass transition temperatures—one for each of the components. To be able to compare melt viscosities, both transitions will have to be taken into account to establish some form of corresponding state. If one accepts the fact that the apparent second-order transition temperature (21) corresponds to a given viscosity (approximately 10^{11} to 10^{12} poises (22)) then the viscosity of a graft copolymer at a given temperature should depend, in the same fashion as the second-order transition, on composition and graft frequency.

There is, however, a second effect governed by the activation energy of viscous flow, which can inverse the relation between the viscosities of two products for a given temperature. The activation energy of the viscosity is a function of intermolecular forces and molecular rigidity caused by the lateral grafted groups (21). A similar influence will be exercised on the apparent second-order transition temperature, i.e., an increase in rigidity and interaction in general will raise T_g.

Job and Lebel (14) made a systematic investigation of the flow behavior of:

(I) poly(vinyl chloride-*g*-styrene-*co*-maleic anhydride)
(II) poly(styrene-*co*-maleic anhydride-*g*-vinyl chloride)
(III) blends of poly(styrene-*co*-maleic anhydride) and poly(vinyl chloride)

The viscosity, activation energy of viscous flow, and T_g, were measured as a function of composition and grafting frequency. These polymers (at least in the blend) are stated to be incompatible. This system is therefore probably applicable to other systems—at least in a qualitative sense.

The following conclusions were reached:

1. T_g, as measured by the torsional modulus, increases with the styrene–maleic anhydride content.
2. For the same composition, T_g is higher the longer the grafted chains (and consequently for fewer grafting points).
3. T_g is independent of type, thus type (I) and type (II) have a similar T_g for the same composition.

These effects follow in a qualitative sense the prediction that an increase in interaction and side group rigidity will cause a corresponding increase in T_g.

4. The activation energy of viscous flow increases with the content of styrene–maleic anhydride.

5. For the same composition, the activation energy is higher for a larger number of shorter chains than for fewer long side chains.

6. The mixtures (type (III)) have a T_g equal to poly(vinyl chloride) except when the mixture is prepared such as to give a molecular dispersion. The second-order transition then becomes equivalent to the corresponding graft.

These observations have consequences of practical importance. The viscosity is thought to answer a relation of the form

$$\eta = \mathrm{A}\ [\exp\ (-\ E/RT)]$$

i.e., the higher the activation energy the faster the decrease in viscosity.

Thus, if we have two graft copolymers A and B, where A has the higher content of maleic anhydride, then

$$T_g\mathrm{A} > T_g\mathrm{B}$$

and at T_gA

$$\eta_{\mathrm{A}} > \eta_{\mathrm{B}}$$

but when, for example, the grafted chains in A are very short, the activation energies E are related as

$$E_{\mathrm{A}} \gg E_{\mathrm{B}}$$

so that

$$\eta_{\mathrm{A}} < \eta_{\mathrm{B}}$$

at a temperature higher than T_gA.

This has been shown to be true by Lebel and Job. Berlin and co-workers (23) in earlier work on poly(vinyl chloride-*g*-butyl methacrylate) and poly(butyl methacrylate-*g*-vinyl chloride) arrived at some preliminary conclusions, but omitted to notice the effect of chain length. Tentatively, one could conclude from Lebel and Job's work that the insensitivity of the rheology to the type of graft (I or II) is caused by the entanglement of chains. Presumably, if type A chains entangle with type A and only a little B, and type B chains with type B chains and only a little A, the macroobservable effect cannot distinguish between A grafted on B or B grafted on A. If, however, A or B are too short for entanglement, an effect of the type of graft should be observed (and was by Berlin, 23).

Rieke (15) measured the melt viscosity and activation energy for viscous flow for poly(ethylene-*g*-acrylic acid) for an acrylic acid content of 8.2%. He reported only minor deviations from base polymer properties in this respect. Suzuki (239) gave detailed melt flow data of poly(ethylene-*g*-vinyl acetate).

It is unfortunate that most researchers used thermomechanical methods (Kargin and Sogolova, 24) to determine flow points, since this method does not give any reliable rheological information. There is, however, a large body of information available based on Kargin and Sogolova's method, particularly in the Russian literature and since it contains some rather basic information on the behavior of grafts, it will be reviewed separately.

C. Thermomechanical Properties

Kargin and Sogolova (24) characterize polymers by thermomechanical curves, constructed on the following principle: the sample, in the form of a molded plaque is heated at a constant rate and subjected to a load applied by a plunger of a given diameter, and the penetration of the plunger is measured over a given time at a given frequency. The curves obtained are a plot of the penetration (usually expressed by the symbol ϵ or ΔL) as a function of temperature. Kargin (25) recently reviewed the behavior of bulk properties of grafts, based on the work of Plate (26–28) and coworkers in Moscow. Kargin is strongly aware of the importance of structure and phase separation in graft copolymers. Consequently, the examples chosen were based on a large dissimilarity of the base and grafted chains, such as starch-*g*-poly(styrene) (26), starch-*g*-poly(methyl methacrylate) (27), poly(vinyl alkalate-*g*-styrene) (28) poly(acrylic acid-*g*-styrene) (28). (See Fig. 15).

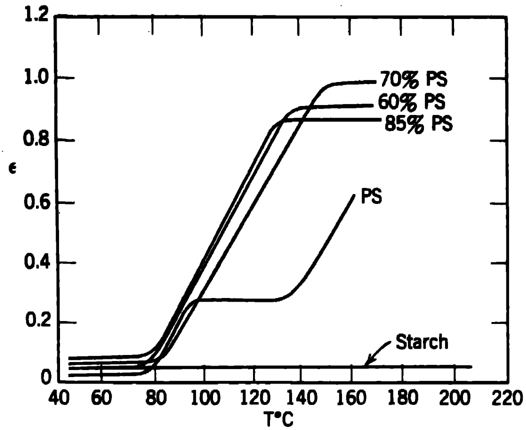

Fig. 15. Thermomechanical curves for poly(styrene) (PS), starch, and starch-*g*-poly(styrene) for various compositions (25).

Similarly, Jendrychowska-Bonamour (29) studied poly(ethylene-*g*-acrylonitrile) and poly(styrene-*g*-acrylonitrile). Each of these polymers has constituent chains which are incompatible when at very low levels of grafting.

Starch has no transition in the region from 40–200°C. Poly(styrene) and the poly(styrene)–starch graft copolymers show a transition at 80°C which changes very little with the grafting ratio. Poly(styrene) shows a flow point at approximately 130°, but none of the grafts show a tendency to viscous flow up to decomposition.

A similar behavior was found for starch-*g*-poly(methyl methacrylate) (27) and amylose-*g*-poly(methyl methacrylate) (27). (See Fig. 16.)

The methyl methacrylate grafts behave differently to some extent, the homopolymer PMMA having a lower glass transition. No flow point could be detected, but a rather broader "elastic" region is shown before decomposition.

The behavior of poly(vinyl alcohol-*g*-styrene) is depicted in Fig. 17. Again there is no flow even at relatively high grafting ratios.

All three examples shown exemplify systems having incompatible components, which therefore show microseparation—regions of different phase being held together by chemical bonds. The thermomechanical properties are largely additive.

Kargin (30) investigated the limits of this additivity by specifically changing the glass transition temperature by the addition of a plasticizer

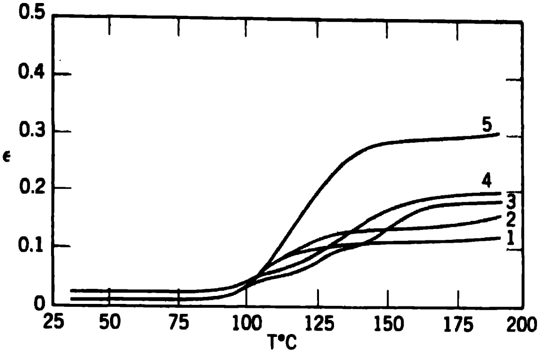

Fig. 16. Dependence of deformation on temperature of amylose-*g*-poly(methyl methacrylate) and starch-*g*-poly(methyl methacrylate) (25): (1) starch; (2) starch copolymer with 80% PMMA; (3) PMMA; (4) starch copolymer with 88% PMMA; (5) amylose copolymer with 80% PMMA.

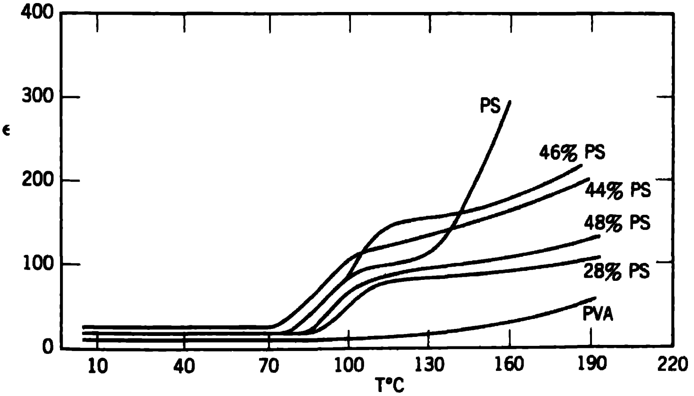

Fig. 17. Dependence of deformation on temperature of poly(vinyl alcohol-*g*-styrene) for various compositions (25).

for either or both of the components. Thus for poly(vinyl alcohol-*g*-styrene) (52:48) tetraline is a plasticizer for polystyrene chains and glycerol for poly(vinyl alcohol) chains. The effect of the addition of tetraline is shown in Fig. 18.

The second-order transition temperature of the poly(styrene) chain is directly proportional to the tetraline content as shown in Fig. 19. The second inflection representing the melting of the poly(styrene) shows the

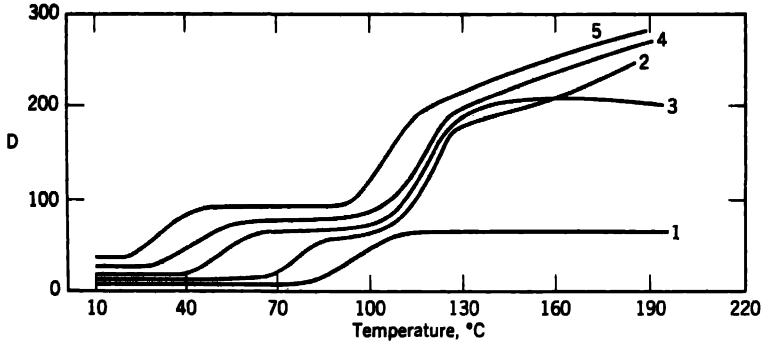

Fig. 18. Plasticization of poly(vinyl alcohol-*g*-styrene) (52:48) with tetraline (25): (1) pure copolymer; (2) 16% tetraline; (3) 20% tetraline; (4) 26% tetraline; (5) 35% tetraline.

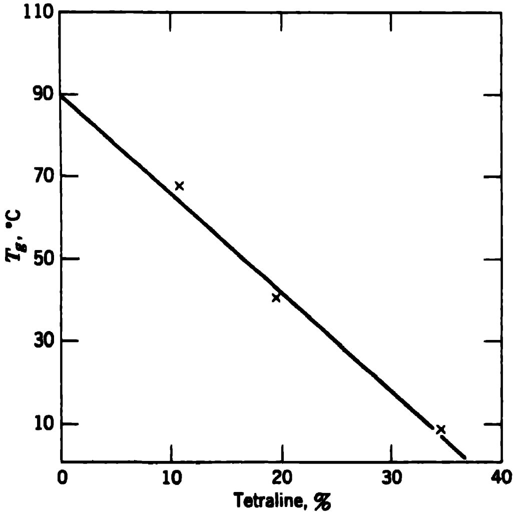

Fig. 19. Glass temperature of poly(vinyl alcohol-*g*-styrene) (52:48) plasticized with tetraline (25).

reduction of the melting temperature. There is also some sign of fluidity previously absent (Fig. 18).

Similarly, if glycerol is added, a specific plasticizer for poly(vinyl alcohol), a decrease of the corresponding T_g results, becoming constant at about one mole of glycerol per two poly (vinyl alcohol) hydroxyl groups (Fig. 20).

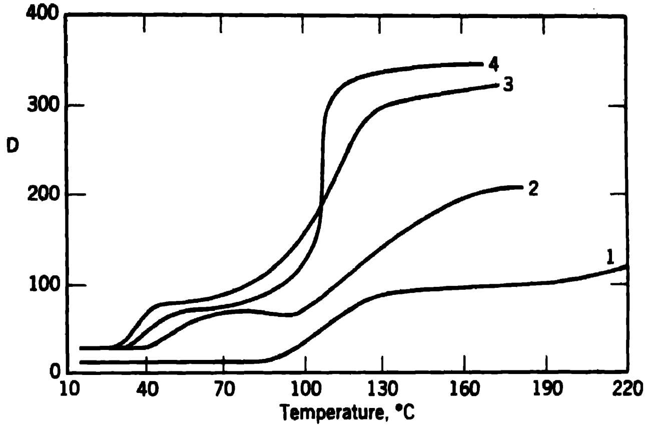

Fig. 20. Plasticization of poly(vinyl alcohol-*g*-styrene) (52:48) with glycerol (25): (1) pure copolymer; (2) 20% glycerol; (3) 25% glycerol; (4) more than 30% glycerol.

The marked second inflections do not shift on addition of either plasticizer, which probably reflects the elastic properties of the backbone polymer component which is not affected by the plasticizer. It is also characteristic of this type of graft copolymer that addition of only one type of plasticizer converts them into a viscous fluid. However, both transitions can be shifted so as to obtain a viscous fluid by simultaneous addition of two plasticizers, specific for each of the components. This is demonstrated in Fig. 21, curve 6.

The effect of each plasticizer acts independently. Similar effects have been shown for poly(acrylic acid-*g*-styrene) (Kargin, 30). If, however, the backbone and side chains do not show a large difference, but are compatible or nearly so, then there is no difference between the glass transition temperatures of mixtures or graft copolymers, as has been demonstrated by Kargin (25). Similar work was carried out by Usmanov (41) on PVC and PS grafts with acrylonitrile, thus confirming these results.

It can be anticipated from the effect of microphase separation that certain regions may be formed richer in one of the components, these regions being visible by the electron microscope. Kargin (31–33) and coworkers demonstrated this effect for the graft copolymer, poly([iso]styrene-*g*-[a]styrene).

The thermomechanical curves for this polymer are shown in Fig. 22.

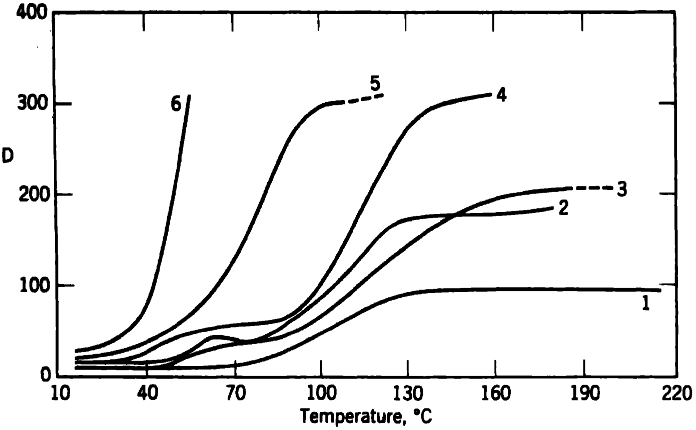

Fig. 21. Plasticization of poly(vinyl alcohol-*g*-styrene) (52:48) with tetraline and glycerol (25): (1) pure copolymer; (2) 20% tetraline; (3) 20% glycerol; (4) 25% glycerol; (5) 20% glycerol and 20% tetraline; (6) 25% glycerol and 20% tetraline.

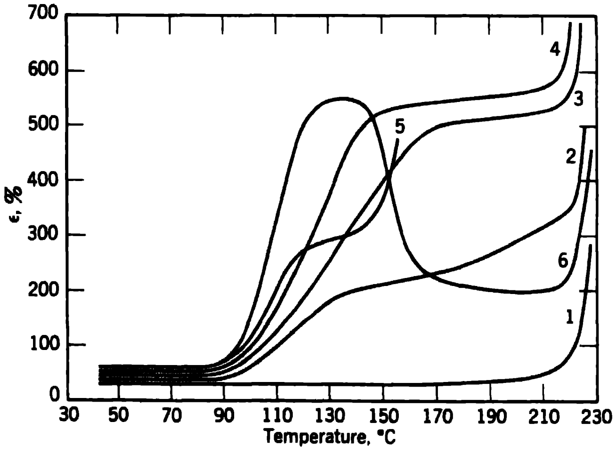

Fig. 22. Dependence of deformation on temperature of: (1) crystalline isotactic poly(styrene); (2) heterogeneous graft copolymer with 17% atactic poly(styrene); (3) heterogeneous graft copolymer with 31% atactic poly(styrene); (4) heterogeneous graft copolymer with 35% atactic poly(styrene); (5) pure atactic poly(styrene); (6) amorphicized isotactic poly(styrene) (25).

The picture again is characteristic of other heterogeneous graft copolymers. Isotactic poly(styrene) is capable of forming a complete series of intermolecular structures up to single crystals. According to the thermomechanical curves, the polymers are heterogeneous in phase and, notwithstanding the chemically identical backbone and side chains, they still show the previously discussed behavior. The samples, however, are more sensitive to heat history as can be seen from Fig. 23.

Grafting in this case did not seriously interfere with the crystallinity of the backbone. The general retardation of the crystallinity rule is, however, demonstrated by some thermomechanical curves of nylon 6-*g*-poly(ethylene oxide) (Kargin, 25; Fig. 24).

Two transitions are shown, but the reduction of the nylon 6 melting point by grafting (second inflection) is a new phenomenon. X-ray investigations showed a complete inhibition of ethylene oxide crystallinity in the graft, while in a blend both components crystallize.

Merrill (34) presented a similar behavior for poly[2,2-bis(4-hydroxyphenyl propane-*b*-ethylene oxide)]. In this case the crystallinity of the poly(carbonate) chain was increased by the insertion of ethylene oxide blocks. Jendrychowska (29) confirmed Kargin's analysis as can be seen from Figs. 25 and 26.

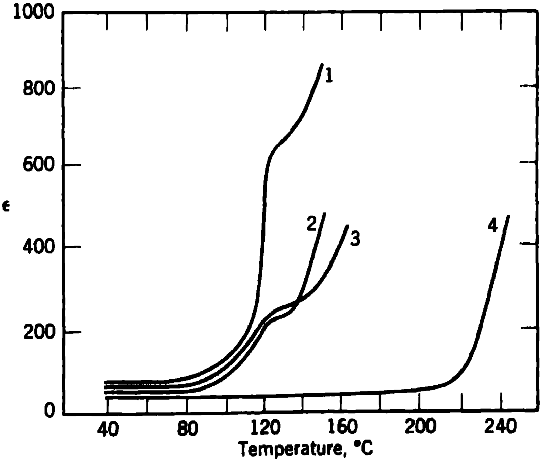

Fig. 23. Dependence of deformation on temperature of: (1) atactic poly(styrene); (2) molecularly grafted copolymer with 85% atactic poly(styrene) after annealing; (3) molecular grafted copolymer with 85% atactic poly(styrene) before annealing; (4) crystalline poly(styrene) (25).

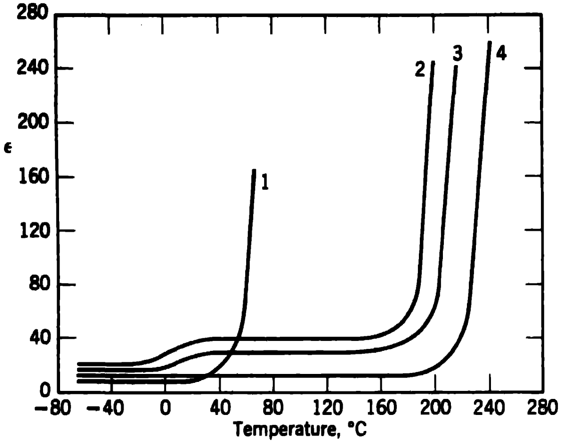

Fig. 24. Dependence of deformation on temperature of nylon 6-*g*-poly(ethylene oxide): (25) Curve (1) poly(ethylene oxide); (2) nylon 6-*g*-poly(ethylene oxide) 44% PEO; (3) 6-*g*-poly(ethylene oxide) 55% PEO; (4) nylon 6.

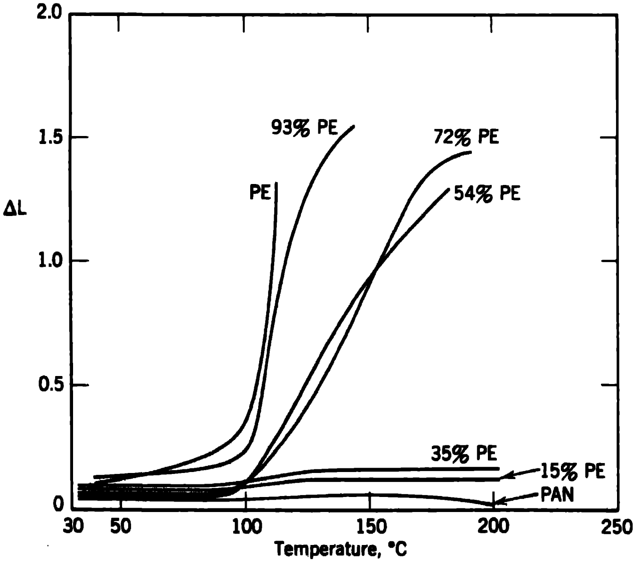

Fig. 25. Thermogravic curves for poly(ethylene)(PE), poly(acrylonitrile) (PAN), and poly(ethylene-*g*-acrylonitrile) (29).

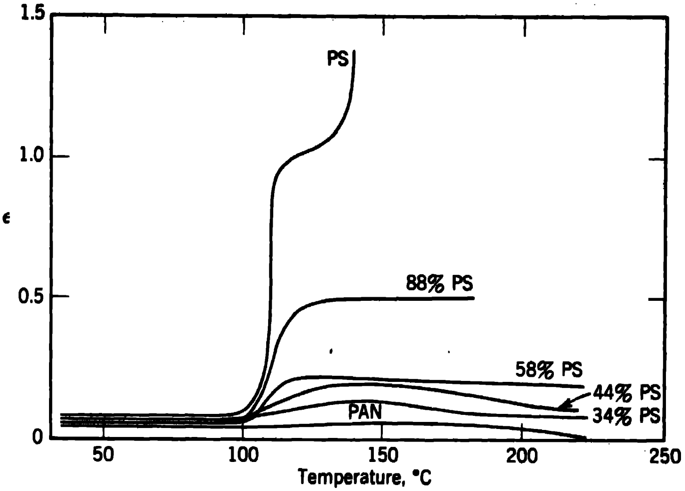

Fig. 26. Thermogravic curves for poly(styrene)(PS), poly(acrylonitrile) (PAN), and poly(styrene-*g*-acrylonitrile) (29).

In both cases the second-order transition of poly(styrene) and the melting point of poly(ethylene) is retained. Neither of the grafts show viscous flow. A number of other graft copolymers have been studied with similar or analogous effects. For example: poly(trifluorochloroethylene-*g*-styrene), Korshak (35); poly(trifluorochloroethylene-*g*-methyl methacrylate), Korshak (35); poly(ω-hydroxyenanthic acid methacrylate-*g*-styrene), Kolesnikov (35); poly(ω-hydroxyenanthic acid methacrylate-*g*-vinyl acetate), Kolesnikov (36); poly[styrene-*co*-*N*-(ω-carboxy-*n*-hexyl)methacrylate-*g*-ω-hydroxyenanthic acid], Gurgenidze (37); poly(ethylene sebacite-*g*-methyl methacrylate), Kolesnikov (38); poly(pentamethylene thiodivalerate-*g*-methyl methacrylate), Kolesnikov (38); poly(styrene-*g*-acrylonitrile), Usmanov (39); poly[(vinyl chloride-*co*-1,2-dichloroethylene)-*g*-acrylonitrile], Usmanov (39); cellulose triacetate-*g*-poly(methyl acrylate), Kozlov (40); poly(styrene-*g*-acrylonitrile), Usmanov (41); poly(vinyl chloride-*g*-acrylonitrile), Usmanov (41); poly[(vinyl chloride-*co*-1,2-dichloroethylene)-*g*-acrylonitrile), Usmanov (41); poly(vinyl alcohol-*g*-styrene), Tsuji (42). The general rules established by Kargin and exemplified above are amply confirmed by these authors on a large variety of copolymers.

The loss of flow of graft copolymers with incompatible constituents seems to be general and the constituent chains can be plasticized individually. This is a characteristic of this group of polymers, which, so far, has not found wide acceptance.

D. The Second-Order Transition Temperature of Graft Copolymers

The glass transition temperature of a polymer is usually associated with the ability of polymer chain segments to move or rotate. A number of theories have been put forward, based on statistical principles or the more recent concept of fluid structure. These are, however, beyond the scope of this work. It is useful, however, to reiterate some of the general principles that have been accepted for some time and test these principles against some of the known data on graft copolymers. At the glass temperature, chain segments of polymer molecules begin to participate in the general kinetic agitation. The coefficient of thermal expansion, as well as the heat capacity and the thermal increment of the refractive index, change sharply at T_g.

Taken together, these facts suggest a close connection between the glass transition and the free volume of a polymer. Fox and Flory (43) and Ueberreiter and Kanig (44) have suggested that, since the free volume increases with rising temperature due to the thermal expansion, the glass transition will occur when the fraction of the total volume which is free volume reaches a certain critical value. Although the complete generality of this *isofree volume* concept of the glass transition is now open to question there is no doubt that the transition temperature and the free volume fraction are intimately connected. Any factor which controls the free volume of a polymer at constant temperature affects the value of T_g. Such factors can be either chemical or physical in nature, but this division becomes diffuse when mainly physical changes, such as crosslinking, also introduce a chemical modification. The main factors influencing T_g are discussed in the following subsections *1* and *2*.

1. *Structure of Grafted Chains*

T_g is affected by size and polarity of side groups and the mobility of the chain. Any factor disturbing the closest packing of the main chain will lower T_g; any factor stiffening or increasing the interaction between chains will increase T_g.

These general principles should apply to graft copolymers. The majority of these polymers have relatively few graft chains, insufficient to affect the free volume available to the backbone, and the T_g of the backbone will initially be the same as for the homopolymer. This was experimentally confirmed in numerous publications and has been demonstrated in a previous section. A transition of the grafted chain will be found as the length of this chain increases, and will be a function of the molecular weight according to the expression (Ueberreiter and Kanig, eq. 1, 44; Fox and Flory, eq. 2, 43, 45)

$$\frac{1}{T_g} = \frac{1}{T_g^{\infty}} + \frac{A}{M} \tag{1}$$

or

$$T_g = T_g^{\infty} - \frac{K}{M} \tag{2}$$

relating the glass transition T_g of a polymer chain to the glass transition at infinite molecular weight T_g^{∞} and M the molecular weight. A and K are empirical constants.

The lower limit where the side chain will start to show polymeric characteristics has not been set generally, but in poly(cetyl acrylate), for example, the side chain shows an individual transition at 35°C, (Wiley and Braver (46)). For a large number of small side chains an effect similar to that found in a homologous series of acrylate can be expected (47). As the number and size of side chains increase, T_g will become progressively lower.

The effect of incompatibility between component chains is still diffuse. Angelo (48) prepared high molecular weight block copolymers of styrene, butadiene, and isoprene in tetrahydrofuran solution by anionic polymerization techniques employing sodium–methyl styrene initiation. Selected samples were characterized by dilute solution techniques and found to be genuine block copolymers with narrow molecular weight distributions and little composition heterogeneities.

In the case of terblock copolymers, Angelo prepared poly(styrene-*b*-butadiene-*b*-isoprene) and poly(butadiene-*b*-styrene-*b*-isoprene). The results are represented in Fig. 27.

TABLE I

Glass Transition Temperatures of Block Copolymers Derived from Torsion Moduli Experiments

Polymer	Type	T_g, °C	Comment
Poly(styrene)	Homo	100	
Poly(butadiene)	Homo	0	
Poly(isoprene)	Homo	15	
Poly(styrene)-poly (butadiene)	Blend	0 and 100	Opaque film
Poly(styrene-b-butadiene)	SBS	0 and 100	Clear film
	BSB	0 and 100	Clear film

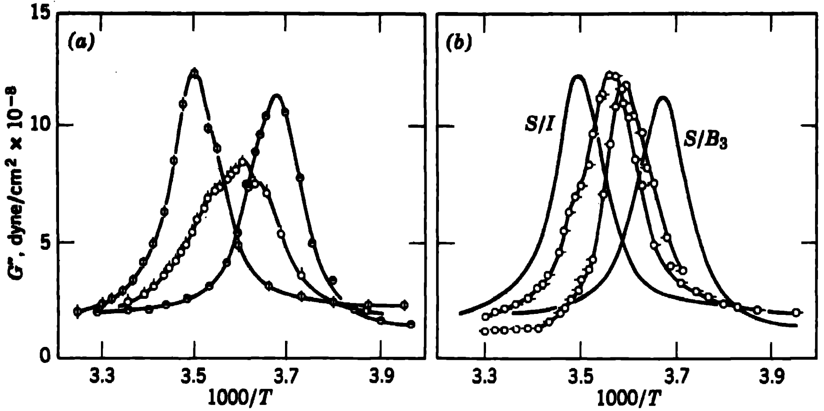

Fig. 27. Loss moduli of terblock copolymers and blends (48): (a) comparison of a blend and two block copolymers; (b) comparison of the block terpolymers and two block copolymers. ϕ, S/I; ȸ, S/B//S/I; ●, S/B_3; ⊖, B/S/I; -○, S/B/I.

S, *B*, and *I* represent poly(styrene), poly(butadiene), and poly(isoprene), respectively. The block polymers are denoted S/B_1, S/B_2, *S/I*, *S/B/I*, etc. The letters identify the polymer segments with the first letter indicating the center segment (e.g., *S/B/I* represents a block terpolymer with polymer segments, *I*∿∿∿*B*∿∿∿*S*∿∿∿*B*∿∿∿*I*).

In Fig. 27*a* the loss moduli for poly(styrene-*b*-butadiene) poly(styrene-*b*-isoprene) are compared with the blend of these two polymers. The data for the first two polymers suggest that one should be able to verify, experimentally, the existence of a double loss peak if two "soft" phases were formed in the physical mixture. Such was not the case. The blend reveals a broad low peak, having structure, which may be explained by assuming that only a portion of the poly(isoprene) and poly(butadiene) segments are able to blend in a single phase.

In Fig. 27*b* the two terpolymers are compared with the same block copolymers as in Fig. 27*a*. Sample S/B/I contained poly(butadiene) and poly(isoprene) segments adjacent to each other on the chain. This proximity provided unhindered phase blending of the two "soft" segments as indicated by the sharp symmetrical peak located between those for the homopolymer phases. In sample B/S/I the center "stiff" poly(styrene) segment separates the two "soft" chains. The loss modulus data show basically one peak, but careful examination reveals that the peak is broader than for S/B/I and a shoulder appears near 10°C (3.5×10^{-3} °K^{-1}). These results indicate imperfect blending of the "soft" chains as influenced by their relative position in the polymer chain.

This relatively detailed work of Angelo confirms the experience with physical mixtures of polyblends (Nielsen, 49,50; Jenckel, 51) and shows that the effects of incompatibility can be extended to block copolymers. Baer (52) prepared some block copolymers representing the opposite case, i.e., blocks of compatible chains poly(styrene-*b*-α-methylstyrene-*b*-styrene), poly(α-methylstyrene-*b*-styrene-*b*-α-methylstyrene) and also the opposite of the spectrum poly(ethylene oxide-*b*-styrene-*b*-ethylene oxide).

TABLE II
Glass Transitions of Block Copolymers

Polymer	T_g °C	Comment
Poly(styrene-*b*-methyl methacrylate)	110 and 133	Incompatible, two transitions
Poly(styrene-α-methylstyrene-styrene)	140–155	Compatible, one transition
Poly(α-methylstyrene-styrene-methylstyrene)	140–155	Compatible, one transition
Poly(α-methylstyrene)	180	Homopolymer
Poly(styrene)	115	Homopolymer
Blend poly(styrene) and poly-(α-methylstyrene)	145	Compatible, one transition
Poly(styrene-*co*-α-methylstyrene)	135	Compatible, one transition
Poly(styrene-*b*-ethylene oxide)	110 and −49	Incompatible, two transitions

Again Baer found that optical clarity of polymer films does not necessarily mean compatibility, nor do opaque films mean incompatibility. It appears that microphase separation cannot be judged solely by optical inspection of a bulk sample of the polymer.

Rembaum and co-workers (53–55) carried a similar type of experimentation into a widely varied field of block copolymers without substantially altering the principle of the evidence so far submitted. Rembaum (54) extended the investigation to poly(4-vinylbiphenyl-*g*-ethylene oxide) and poly(2-vinyl naphthalene-*g*-ethylene oxide) (coded PVB-*g*-PEO and PVB-*g*-PEO).

The PVN–PEO system shows a "well" in the intermediate zone of the modulus–temperature curves (see Fig. 28).

This "well" is characteristic for both blends and grafts and was attributed by Rembaum to the differences in mobility and compatibility with PEO of PVN chains on either side of T_g. Also specimens annealed above 120°C

TABLE III

Polymer	T_g °C	T_m °C	Comment
PEO	-	65	Crystalline homopolymer
PVB	154	-	Amorphous homopolymer
PVN	148	-	Amorphous homopolymer
PVB-*g*-PEO	130–150	65	Two independent transitions
PVB-*b*-PEO	130–150	65	for two-phase systems
PVB, PEO blend	130–150	65	
PVN-*g*-PEO	65	120	Anomalous behavior; see text
PVN, PEO blend	65	120	

and then cooled to below 65°C did not show crystallities of PEO. The explanation given by Rembaum is only tentative, but could be a manifestation of a more general nature in incompatible systems, in which at least one of the partners is crystalline.

A more extensive investigation by Rembaum (56) and co-workers found that poly(vinylnaphthalene) and poly(ethylene oxide) (54:46% by weight) form homogeneous blends or grafts when prepared under conditions which

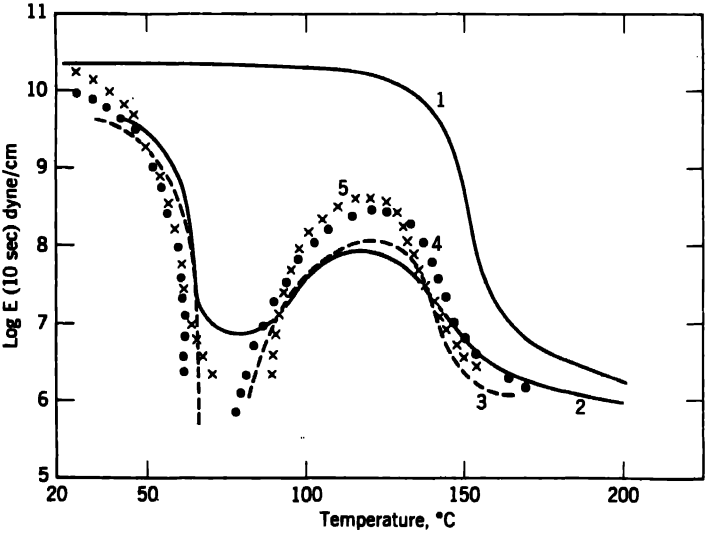

Fig. 28. Torsional modulus as a function of temperature for: (1) pure PVN; (2) PVN–PEO graft (PVN 25%, PEO 75%, $\bar{M}_w$ of PVN ≃ 950,000); (3) PVN–PEO blend (PVN 25%, PEO 75%, $\bar{M}_w$ of PVN ≃ 950,000); (4) PVN–PEO blend (PVN 40%, PEO 60%, $\bar{M}_w$ of PVN ≃ 400,000); (5) PVN–PEO blend (PVN 50%, PEO 50%, $\bar{M}_w$ of PVN ≃ 400,000) (54).

inhibit the crystallization of poly(ethylene oxide). Such preparations can be obtained from solutions in a good solvent for both components, either by precipitation which lead to coacervation rather than fractionation or by freeze-drying. Preparations containing more than 46% w/w were characterized by modulus versus temperature curves exhibiting a minimum at 60°C. This behavior was interpreted as due to microphase separation taking place with increasing temperature, a process which becomes irreversible at about 120°C. A graft copolymer having 54–46 composition was rubbery at room temperature and, in contrast to polyblends, did not exhibit the poly(vinylnaphthalene) glass transition at 138°C. Similar properties could not be reproduced in preparations of poly(ethylene oxide) with poly(styrene), poly(4-vinylbiphenyl), or poly(acenaphthylene). These preparations exhibited a behavior characteristic of mixtures of two incompatible polymers.

Moacanin (240) further described blends and grafts of poly(β-vinylnaphthalene) and poly(ethylene oxide) accenting practical application of such polymers. This case, described in some detail, emphasizes the importance of the physical state (crystalline or amorphous) in incompatible grafts and the anomalies that can occur when bistable coexistence interferes.

An interesting example for compatible components is given in a patent (60). In Fig. 29 the properties of a polyester copolymer of PVC are compared by copolymerization of a high molecular weight polyester with a terminal double bond and vinyl chloride. The properties of these copolymers are compared at the temperatures T_1, the temperature at which the polymer consolidates under a pressure of 3200 psi, and T_2, the temperature at which the polymer flows under the same pressure.

The solid lines in Fig. 29 represent the properties of the copolymers as a function of composition while the broken vertical lines give the useful service range for plasticized compositions with DOP (dioctylphthalate), VAC (vinyl acetate copolymer), and EHA (ethylhexyl acrylate copolymer). This represents the case of a constant molecular weight grafted side chain but a variable number of side chains. T_2, the "flow" temperature, is maintained quite well up to 50% polyester content, while T_1, similar to the glass transition temperature, falls more rapidly. Both trends are favorable for a good useful service range, and confirm earlier observations on the flow behavior of graft copolymers. A number of systems have been reported, mostly dealing with incompatible components, without further contributing to the principles established. These have been assembled in Table IV including methods used and other properties measured.

TABLE IV
Physical Properties of Graft Copolymers

Author	Ref.[a]	Polymer system	Method	Properties measured
Shinohara et al.	61	Poly(ethylene), nylon grafted with acrylic acid, acrylonitrile methyl acrylate	Torsional modulus and loss as function of temperature	Dispersion ranges, T_g and T_m, for homo and graft copolymers
Chapiro	62	Poly(tetrafluoroethylene-*g*-styrene)	Various	Simple qualitative mechanical properties
Natta et al.	63	Poly(propylene-*g*-methyl methacrylate) Poly(butene-1-*g*-styrene) Poly(propylene-*g*-vinyl chloride)	Various	Tensile and impact properties
Golubeva et al.	65	Poly[(styrene-*co*-isopropylstyrene)-*g*-methyl methacrylate] Poly[(styrene-*co*-isopropyl styrene)-*g*-acrylonitrile]	Thermomechanical, tensile, thermal	Tensile properties, thermal stability, T_g, T_m
Kargin et al.	66	Starch-*g*-poly(styrene) Starch-*g*-poly(acrylonitrile)	Thermomechanical	T_g, T_m, flow properties as function of composition
Kolesnikov et al.	67	Poly(ethylene sebacate-*g*-methyl methacrylate) Poly(pentamethylene thiodivalerate-*g*-methyl methacrylate)	Thermomechanical, tensile	T_g, T_m, tensile strength, elongation
Landler and Lebel	69	Poly(vinyl chloride) grafted with vinyl monomers	Various	Tensile strength, elongation
Kadonaga et al	72	Poly(propylene-*g*-styrene)	Various	Tensile strength, elongation as function of composition
Usmanov et al.	73	Poly(styrene-*g*-acrylonitrile) Poly(1,2-dichloroethylene-*g*-acrylonitrile)	Thermomechanical and thermal	T_g, T_m, flow point as function of composition thermal stability

Korshak et al.	74	Phenol formaldehyde resin grafted with isophthaloyl chloride and 2,2-bis-(4-hydroxyphenyl)propane	Tensile	Tensile strength, elongation
Korshak et al.	75	Polyamides and polyethers grafted with vinyl monomers	Various	T_g, T_m, tensile properties; thermal stability
Takamatsu et al.	77	Poly(ethylene-*g*-styrene) Poly(ethylene-*g*-methacrylate)	Thermomechanical	T_g, T_m
Korshak et al.	78	Poly(ethylene terephthalate) grafted with vinyl monomers	Various	Tensile strength; elongation, properties pertaining to photographic emulsion carriers
Rieke	80	Poly(ethylene-*g*-acrylic acid)	Various	Crystallinity; elastic modulus; adhesion
Berlin et al.	84	Poly(vinyl chloride-*g*-methylvinylpyridine)	Various	Tensile properties; impact strength as function of composition and temperature
Serganova	85	Amber-*g*-poly(methyl methacrylate)	Various	Optical, tensile properties
Tsuji et al.	86	Poly(vinyl alcohol-*g*-styrene)	Thermomechanical	T_m, T_g
Kolesnikov and Gurgenidze	87	Grafts from polyesters of ω-hydroxyenanthic acid methacrylate with methacryloyltriethyl stannate argermanium	Thermomechanical and x-ray	Crystallinity, T_g, T_m
Mozisek	97	Poly(tetrafluoroethylene-*g*-vinyl acetate)	Various	Tensile properties; adhesion as function of composition and grafting method
Robalewski et al.	98	Poly(ethylene-*g*-vinyl acetate)	Various	Adhesion; other surface properties
Korshak et al.	99	Poly(trifluorochloroethylene) grafted with vinyl monomers	Thermomechanical; tensile	T_g, T_m; tensile strength; elongation

(continued)

TBALE IV (*continued*)

Author	Ref.[a]	Polymer system	Method	Properties measured
Shibaev et al.	101	Poly([iso]styrene-*g*-[a]styrene)	Thermomechanical	T_g, T_m; crystallinity
Korshak et al.	102	Poly(trifluorochloroethylene-*g*-styrene)	Thermomechanical	T_g, T_m; tensile properties
Usmanov	104	Poly(styrene-*g*-acrylamide) Poly(vinyl chloride-*g*-acrylonitrile) Chlorinated PVC-*g*-poly-(acrylonitrile)	Thermomechanical	T_g, T_m as function of composition and plasticizer content
Khismatullina et al.	105	Gelatine grafted with acrylic monomers	Various	Tensile properties; elastic modulus thermal stability
Koslov et al.	107	Cellulose triacetate grafted with methyl acrylate	Thermomechanical	T_g, T_m; viscous flow discussed in comparison and blends
Berlin et al.	108	Polyvinyl chloride grafted with nitrile and vinylpyridine rubbers	Various	Tensile, electrical properties; impact strength
Ide et al.	110	Cellulose acetate grafted with acrylic monomers	Various	Tensile properties; T_g, T_m dynamic viscoelasticity; thermal properties
Movsum-Zade et al.	111	Cellulose triacetate-*g*-poly-(methyl methacrylate)	Thermomechanical	T_g as function of composition number of graft chains and molecular weight of graft chains
Pagani et al.	112	Poly(butene-1-*g*-styrene)	Various	Film properties
Cusano et al.	114	Polyester urethane block terpolymers	Various	Tensile properties; solvent resistance; heat stability
Puett et al.	115	Poly(ethylene-*b*-propylene) crystalline	Various	Elastic properties; "Mullins" effect
Rieke et al.	15	Poly(ethylene-*g*-acrylic acid)	Various	Tensile; elastic properties; rheological behavior adhesion

Baccaredda et al.	57	Poly(styrene)-poly(butadiene)-poly(acrylonitrile)grafts blends and random copolymers	Sound velocity and damping (10 Kc)	T_g for all components as function of composition and temperature
Lebel and Job	14	Poly(vinyl chloride-*g*-(styrene-*co*-maleic anhydride) grafts, copolymers and blends	Torsional modulus and viscosity	T_g, T_m; bulk viscosity
Goldberg	58	Poly(bisphenol A carbonate-*b*-ethylene oxide)	Thermomechanical; flexural; tensile; impact	T_g, T_m; tensile properties
Gurgenidze et al.	37	Grafts from aliphatic ω-hydroxy acids and styrene-[*N*-(ω-carboxy-*n*-hexyl)-methacrylamide]copolymers	Thermomechanical	T_g, T_m; viscous flow as function of grafting frequency and molecular weight
Kolesnikov and Gurgenidze	17	Copolymers of poly(ω-hydroxyenanthic acid methacrylate)-*co*-styrene	Thermomechanical	T_g, T_m as function of composition and molecular weight
Honjo and Ogawa	248	Poly(vinylfluoride-*g*-styrene)	Dynamic; mechanical	α-Dispersion lowered by grafting; β dispersion disappears at a grafting ratio >0.3; styrene grafting in amorphous regions
Newman and Strella	249	Rubber grafts, blends with styrene-acrylonitrile	Tensile	Hypothesis for reinforcement of glassy polymers
Akiyama et al.	250	Poly(ethylene-*g*-acenaphthylene)	Aging	Improved stress cracking

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[a] References arranged in chronological order.

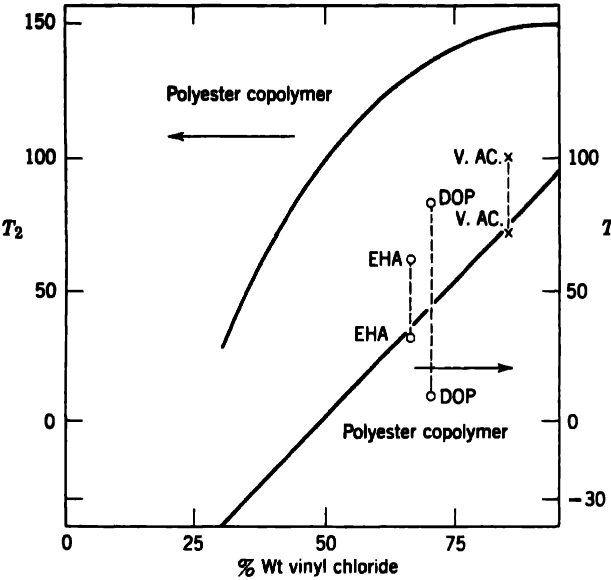
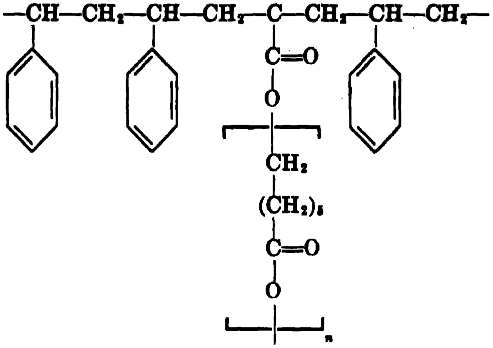


Fig. 29. Transitions for vinyl chloride-polyester graft copolymers and plasticized PVC (see text) (60).

2. Molecular Weight of Grafted Chains

The effect of the molecular weight of the grafted chain has been inferred, but not clearly established experimentally. The relation between T_g and molecular weight for a homopolymer was given in eqs. 1 and 2 (pp. 120, 121). This equation was stated to apply when the second-order transition temperature of the grafted chain could be detected as a separate entity. Experimental confirmation can only be achieved on graft copolymers where the sites of grafting on the main chain and the molecular weight of the grafted chain are under definite control, precluding, therefore, methods depending on a random attack on the backbone.

Some careful work by Kolesnikov (36) will be described in some detail here, notwithstanding the fact that the graft copolymers involved would still show a statistical distribution of molecular weight and branching frequency. Kolesnikov grafted methacrylate modified ω-hydroxyoenanthic acid polyesters (HOEPM) to a poly(styrene) chain by copolymerization, thus obtained graft copolymers of the form,



After careful fractionation he obtained the polymers identified in Table V.

TABLE V
Fractionation of Styrene-HOEPM Copolymers (MW, HOEPM = 6000)

Fraction no.	Yield of fraction (% of wt of unfractionated copolymer)	Elementary analysis (mean), %		η, dl/g	Huggins const.	n/m	Q
		C	H				
1	12.2	92.20	7.95	0.535	0.18	—	—
2	17.2	91.82	7.55	0.475	0.29	0.0137	3420
3	16.5	91.70	7.88	0.455	0.29	0.0176	2660
4	18.5	90.03	7.63	0.440	0.31	0.0741	630
5	12.8	89.40	7.75	0.385	0.44	0.0967	485
6	12.8	87.64	7.85	0.305	0.81	0.1702	275
7	5.1	67.02	9.92	0.230	1.88	15.72	3

The statistical average frequency of branching was calculated from

$$Q = \frac{1}{n/m}\bar{P}$$

where

Q = distance between the grafted HOEPM branches, expressed as the number of styrene units

n/m = ratio of number of polyester repeating units (not including methacrylates) to the number of styrene units in the graft copolymer

$\bar{P}$ = degree of polymerizations of HOEPM

The thermomechanical curves were recorded with the instrument designed by Tsetlin (59) with a load of 100 g and a punch of 4 mm diameter. None of the thermomechanical curves show the two points of inflection typical of mixtures of polymers. (See Fig. 30.)

It is evident from Table V that as the frequency of grafting increases the symmetry of the macromolecules increases, as is shown by an increase in the Huggins constant and simultaneous decrease in η. X-ray analysis showed that the degree of order in the graft copolymer increases with decreasing values of Q, as was found for copolymers of HOEPM and acrylonitrile.

Examination of the thermomechanical properties of the graft copolymers in Fig. 31 indicates that the softening point of the copolymers increases with increasing length of the main chain. This is a result of both the increase in length of the backbone and the increase in the number of interacting branches which is a consequence of the increased length of the backbone. The fact that the length of the main chain of the graft copolymer

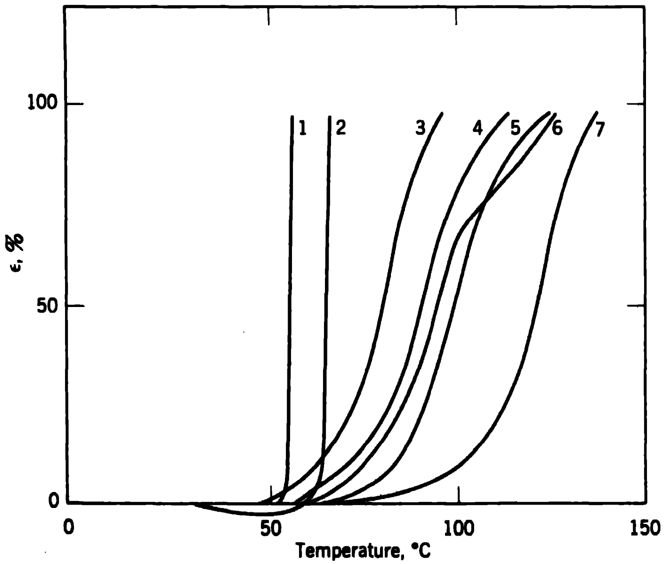


Fig. 30. Thermomechanical properties of graft copolymer fractions of poly(hydroxoenanthate-*g*-styrene) (36). (1) Poly(hydroxoenanthate) (HOEPM); (2) Graft copolymer $Q = 275$; (3) Graft copolymer $Q = 3420$; (4) Poly(styrene); (5) Graft copolymer $Q = 485$; (6) Product of methanolysis of graft copolymer $Q = 485$ and 2660; (7) Graft copolymer $Q = 2660$.

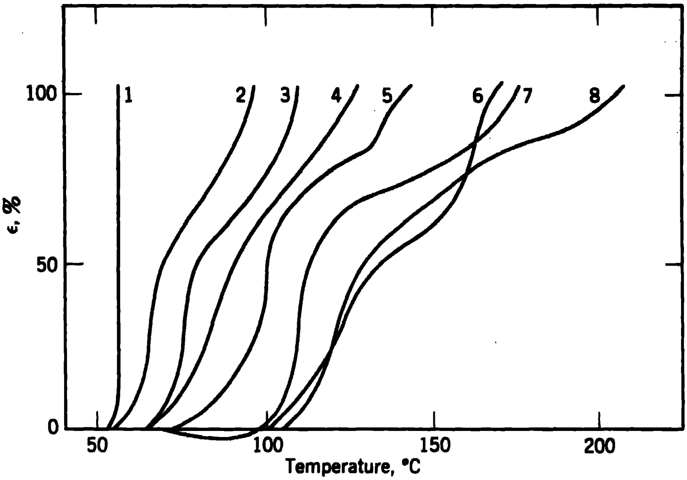


Fig. 31. Thermomechanical properties of graft copolymers of various compositions poly(hydroxoenanthate-*g*-styrene) (36). (1) Poly(styrene); (2) Product of methanolysis of graft copolymer with $[\eta] = 0.28$; (3) Graft copolymer with $[\eta] = 0.28$; (4) Product of methanolysis of graft copolymer with $[\eta] = 0.44$; (5) Graft copolymer with $[\eta] = 0.44$; (6) Graft copolymer with $[\eta] = 1.18$; (7) Product of methanolysis of graft copolymer $[\eta] = 1.18$ and 1.92; (8) Graft copolymer with $[\eta] = 1.92$.

macromolecule influences the thermomechanical properties of the copolymer is indicated by the fact that the thermomechanical properties of the methanolysis products fall off as their intrinsic viscosity decreases. It should be noted that the softening points of the methanolysis products are always below those of the original graft copolymers, consequently the grafting on of polyester side chains brings about (at a given frequency of branching) an increase in the heat resistance of the polymer (See Fig. 32.)

With increasing frequency of grafting, the thermomechanical curves shift toward the lower temperature side. Thus, in the copolymers of HOEPM with vinyl acetate, the polyester branches exert only a plasticizing effect. X-ray examination showed that as the value of *Q* decreases the degree of order in the graft copolymer increases. The evidence presented is not conclusive but indicative of a trend, particularly since it was not made clear if the components were compatible.

Baccaredda (57) determined the dynamic mechanical properties (sound velocity and damping factor) for blends and the corresponding graft copolymers of poly(styrene) and poly(butadiene) as well as the poly(styrene-*co*-acrylonitrile)–poly(butadiene-*co*-acrylonitrile) system. In the

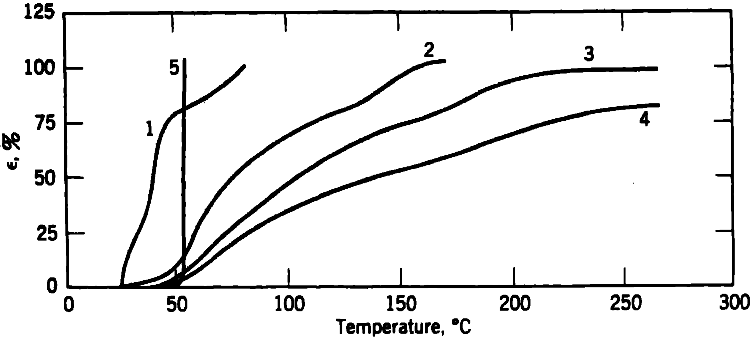


Fig. 32. Thermomechanical properties of poly(hydroxoenanthate-*g*-vinyl acetate) (36). (1) Graft copolymer $Q = 200$; (2) Graft copolymer $Q = 310$; (3) Graft copolymer $Q = 2280$; (4) Poly(vinyl acetate); (5) Poly(hydroxoenanthate).

polyblends the same relaxation phenomena, characteristic of each component, are found located at the same temperature (for a given frequency) as in the pure component. On the other hand, if the degree of branching in the grafted materials is sufficiently high, the relaxation phenomena relative to the base components are shifted toward lower temperatures as compared with the corresponding phenomena relative to the same component in the pure state or in mixture with the grafted component. These shifts are much more marked when the base component is characterized by polar chains or by hydrogen bridges between molecules. These observations are supported with ample experimental evidence; however, Baccaredda does not support his structural ideas with convincing data.

No quantitative rules have as yet been established between the transitions of graft copolymers and molecular parameters. Each case has yet to be judged on the performance of the system studied as has been shown by the representative examples in this section.

E. Mechanical Properties of Graft Copolymers

The bulk properties of graft copolymers are controlled by the same basic principle already discussed, and consequently fall into two classes, (*a*) graft copolymers and compatible constituent chains or low molecular weight grafts, and (*b*) graft copolymers with incompatible constituent chains.

1. *Compatible or Semicompatible Systems*

These systems have few novel properties and can be described by the behavior of the corresponding polyblends (11). Polyblending, however, is a very sensitive process. If the two polymers are completely compatible, the blends and the corresponding grafts behave like an ordinary amorphous polymer with a single transition region and an intermediate glass transition temperature, and obey the law of corresponding viscoelastic states. If the polymers to be blended are quite incompatible (and this is the general case) the polymers do not wet each other and essentially cannot be blended even in a grossly homogeneous fashion. Favorable effects are obtained when the polymers are on the borderline of incompatibility-compatibility, so that a system of two finely divided continuous phases is formed, one phase being rubbery (at room temperature) the other being rigid. Buchdahl and Nielsen (50) described such a system in detail for blends of poly(butadiene-*co*-styrene) copolymers of different composition and with poly(styrene). Such systems are also used for high impact poly(styrene) resins. It is in this region that graft copolymers show surprising differences from polyblends. Of most interest, however, are systems which cannot be polyblended.

The earliest examples of these systems that have reached practical application are the rubber graft systems. These systems were reviewed in some detail by Burlant and Hoffman (5). It is here that the specific advantages of grafts as compared to blends are well established.

Lundstedt (153), for example, demonstrated that the graft copolymer of styrene to rubber had a much better impact strength than the corresponding blends (see Fig. 33). Similar observations were made for rubber aniline–formaldehyde grafts.

One of the most important synthetic rubbers is SBR, a copolymer of styrene and butadiene. The usual commercial product has a butadiene–styrene ratio of about 3:1. Grafts of SBR with styrene have been prepared in a number of ways. The mechanical damping of the graft polymers shows two peaks (Berlin, 155), representing the damping loss of the rubber at −40°C and the polystyrene at 100°C. Ceresa (4) reviewed the properties of some of these grafts. It must be emphasized that most of the work was directed at better compatibility of the constituent chains. Thus, if styrene is grafted on to poly(butadiene-*co*-styrene) the grafted copolymer increases the compatibility of the two homopolymers and the presence of substantial proportions of the elastomer can be tolerated without phase separation and with considerable increases in the impact strength (Hayes 156).

Allen represented the improvements to be obtained by grafting in Table VI. It must be noted, however, that tensile strength in general is

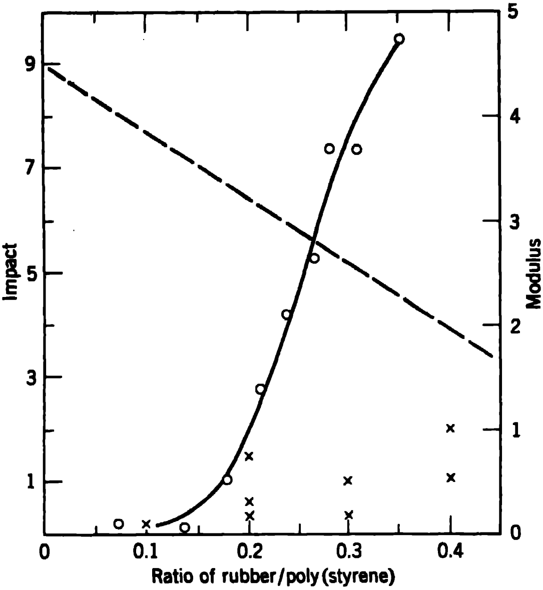


Fig. 33. Comparison of impact resistance of Hevea-*g*-poly(styrene) (○) and homopolymer blends (×) (153).

lower than for the corresponding homopolymers. Liquid poly(butadienes) have been used to serve as a backbone for grafts. It is interesting to compare the effect of using a copolymer backbone with a poly(butadiene) backbone. Properties of the latter type grafts and blends are given in Table VII.

The improvement in impact strength is not as great as that obtained by using poly(butadiene-*co*-styrene) as the base polymer for the grafting reaction. Again the tensile properties are adversely affected. It is surprising to see, therefore, that grafts of aniline–formaldehyde to SBR show a definite improvement in tensile properties (van Alphen, 154) as set out in Fig. 34.

Other examples of the improvement of properties due to grafting in the region of doubtful compatibility of constituent chains can be found among the ABS polymers, now of commercial importance. Baccaredda (57) for example treated poly(styrene-*co*-acrylonitrile)-*g*-(butadiene-*co*-acrylonitrile) in some detail (see Chapter IV, Section 3). He found from the observation of sound velocity on damping in mixtures and corresponding grafts, that the graft had improved impact strength. A rather extensive patent literature dealing with this subject will not be treated in detail in this book.

TABLE VI

Physical Properties of Compositions Containing Poly[(butadiene-*co*-styrene)-*g*-styrene](157)

Plasticizer		Butadiene-styrene copolymer			Styrene-grafted butadiene-styrene copolymer		
Weight poly[(butadiene-*co*-styrene)-*g*-styrene], %	0	0	0	0	12.1	24.2	36.3
Weight poly(butadiene-*co*-styrene), %	0	10	20	30	0	0	0
Weight polystyrene, %	100	90	80	70	87.9	75.8	63.7
Izod impact strength (ft lb/in. of notch) (ASTM D256) 25°C	0.6	1.0	3.6	4.4	2.7	7.6	8.8
−29°C	0.5	0.5	0.7	1.4	1.0	1.8	5.0
−40°C	0.4	0.3	0.6	0.9	0.6	1.7	3.2
−51°C	0.2	0.3	0.4	0.4	0.4	1.0	2.4
Tensile strength, psi (ASTM D638)	7,200	5,500	3,800	2,500	4,800	3,700	2,700
Flexural strength, psi (ASTM D790)	16,600	12,000	8,600	6,400	11,600	8,500	5,000
Flexural modulus, ($\times 10^{-5}$) (ASTM D790)	5.1	4.1	3.6	2.9	4.2	3.2	3.0
Elongation at break, % (ASTM D638)	2	4	8	10	16	24	31
Heat distortion point, °C (ASTM D648)	87	86	81	80	84	84	82
Dielectric constant at 10^6 cps (ASTM D150)	2.5	—	2.5	—	—	2.5	—
Weight water absorption: 10 days immersion (%)	0.1	—	0.4	—	—	0.2	—

Other examples may be derived from the surface coating field. Melrose and Solomon (158) achieved plasticization of styrene–butadiene copolymers by grafting with methylol acrylamide, where polymeric blends were not suitable. The compatible or semicompatible systems are therefore a region in which grafts have decided advantages over polyblends and should develop further in the near future.

TABLE VII
Impact Properties of Poly(butadiene-*g*-styrene) (156)

Blend wt styrene monomer-liquid poly(butadiene) %	Type liquid poly(butadiene)	Type blend[a]	Tensile properties				Flexural properties		Izod impact strength	Clash-Berg[b] °C		
			Yield		Break							
			psi	Elongation %	psi	Elongation %	psi	Deflection in.	ft lb/in. of notch	T_t	T_{2000}	SR
100.0– 0	—	—[c]	—	—	8,000	2.5	16,000	0.2	0.5	90	102	12
97.5– 2.5	A	P	—	—	8,567	5.0	16,336	0.42	1.2	90.1	102.6	12.5
95.0– 5.0	A	P	—	—	8,140	5.0	15,565	0.72	0.93	88.7	101.7	13.0
90.0–10.0	A	P	7,153	5.0	6,228	6.5	13,502	0.75	0.43	83.4	99.6	16.2
97.5– 2.5	A	M	—	—	8,375	4.8	16,765	0.32	0.67	88.2	102.1	13.9
95.0– 5.0	A	M	—	—	8,150	3.8	15,623	0.26	0.60	83.1	98.0	14.9
97.5– 2.5	B	P	—	—	9,065	5.0	16,464	0.64	1.2	Not determined		
95.0– 5.0	B	P	—	—	9,127	5.0	16,807	0.29	0.86	Not determined		
90.0–10.0	B	P	—	—	7,975	3.9	15,224	0.18	0.33	Not determined		

[a] P = polymerization blend (styrene monomer polymerized while containing liquid poly(butadiene); M = mechanical blend (liquid poly(butadiene)) incorporated into preformed polystyrene, on mill rolls). [b] Clash-Berg = stiffness versus temperature (*Ind. Eng. Chem.*), **34**, 1218 (1942); T_t = brittle temperature, stiffness modules 135,000 psi (approximate softening point); T_{2000} = rubber temperature, stiffness modulus 2,000 psi. [c] Commercial bulk polymerized poly(styrene); typical properties given.

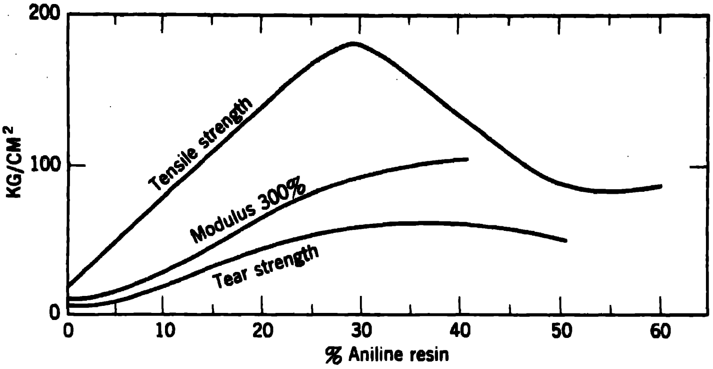


Fig. 34. Strength properties of SBR containing aniline-formaldehyde (154).

2. *Incompatible Systems*

In incompatible systems the properties vary in a less predictable manner. Careful consideration has to be given to all factors influencing the physical properties of a graft. If, for example, grafting disrupts the crystallites, the strength may decrease despite a reinforcement by the copolymer. This was observed by Sella and co-workers (161) with poly(tetrafluoroethylene-*g*-styrene) and Myers (160) with poly(ethylene-*g*-styrene) and poly(ethylene-*g*-acrylonitrile). Bachman and Heisey (162) tabulated the values shown in Table VIII.

Similarly, Burlant and Taylor (163) investigated poly(ethylene-*g*-acrylonitrile) and found the values given in Table IX. In this case the strength increases with increasing grafting ratio, probably because the acrylonitrile crystallinity contributed appreciably to the physical properties. This was confirmed by Myers (160) and Chapiro (164).

TABLE VIII
Tensile Properties of Poly(ethylene) Films Grafted with Styrene

Wt % of grafted monomer	Tensile strength, psi	Ultimate elongation, %	Initial modulus of elasticity, psi
0	2480	700	17,400
2.0	2450	655	17,500
5.3	2340	605	20,300
11.3	2220	535	22,300
20.8	1700	4.5	30,400
30.4	1590	275	34,200
Poly(styrene)	5000–9000	1.0–2.5	4–5 × 10^5

TABLE IX

Physical Properties of Linear Poly(ethylene) Film Grafted with Acrylonitrile*

Wt % of grafted monomer	Density	Tensile strength, psi (average of values in machine and traverse direction)
0	0.944	4136
12	0.965	4780
60	1.015	5120
140	1.058	6950
214	1.076	7950

* Initial film thickness = 2 mil

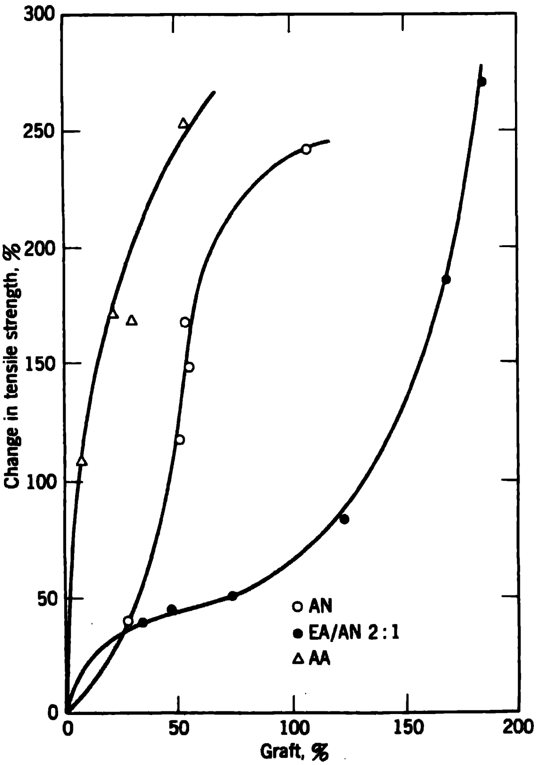


Fig. 35. Change in tensile strength of cellulose grafted with: AN = acrylonitrile; EA/AN 2:1 = ethyl acrylate-acrylonitrile random copolymer; AA = acrylamide (165).

A similar effect was observed from cellulose grafted with acrylonitrile or acrylonitrile copolymers. Schwab (165) found the figures graphically represented in Fig. 35.

Another complication is caused by crosslinking, often suspected or observed as a result of grafting. In this case the tensile strength and modulus increase, as the elongation decreases (Mesrobian, 166; Miller, 167; Pinner, 168).

A combination of all these factors—compatibility, crystallinity, crosslinking, and chemical bridging—may be found in a group of block and graft copolymers usually not discussed in this regard, i.e., urethane-linked polymers. Many of these are true block or graft copolymers. It is beyond the scope of this work to discuss this extensive group of materials and the reader is referred to two books on this subject (169, 170).

Kolesnikov (171) grafted complex polyester chains onto poly(methyl methacrylate) by transesterification. The mechanical properties of these (incompatible) grafts followed the general pattern: a decrease of tensile strength with increasing content of the graft chain. A similar effect is generally noted in the references assembled in Table IV, p. 000 (physical properties of graft copolymers) and in most of the grafting work on fibrous bases assembled in Tables XII and XIII.

Battaerd and Tregear (159) investigated a number of graft copolymers derived from poly(vinyl chloride). The graft copolymers were obtained by radiation of the appropriate monomer/polymer mixtures based on a commercial granular PVC with a *K* value of 65. Incompatibility was judged in the first instance by visual observation of turbidity in films prepared from the graft copolymers. In the case of *n*-butyl methacrylate grafts no turbidity could be observed, but phase separation could be deduced from the physical properties measured. The significant data have been assembled in Table X.

Using simple thermodynamics, compatibility can be calculated using Scatchard's equation and published values for the cohesive energy density. Considering the extensive approximations used, theoretical and experimental data show reasonable agreement.

Tensile strength, Young's modulus, and Vicat softening points were plotted as a function of composition for these graft copolymers. All these curves show a change in slope, a maximum or a minimum close to the predicted point of phase separation. In all cases tensile strength decreases with increasing graft content beyond the point of incompatibility. Again the most useful properties seem to lie in the region of doubtful compatibility.

TABLE X (159)

Series code	Monomer grafted	Composition range wt %	Est. no. of grafting sites per molecule of PVC	Mol. wt range of grafted chains	Theoretical prediction of phase separation		Observed position of phase change	
					% grafted polymer	Mol wt of graft chain	% grafted polymer	Mol wt of graft chain
M	Methyl methacrylate	1.32–37.1	4.18×10^{-2}	12,540–493,800	>1.3	>10,000	1.32% polymer chains phase separation	Separation apparent at 12,540
V	Vinyl acetate	0.40–39.2	5.60×10^{-2}	1,326–359,600	>8.5	>55,500	Between 2.8 and 15.8%. Polymer at 8.5% just showing signs of phase separation	Between 14,000 and 127,000 starting at 55,500
E	Ethyl acrylate	0.54–39.5	7.16×10^{-2}	4,700–570,800	>0.8	>7,500	Between 0.5 and 2.1%	Between 4,700 and 18,690
B	*n*-Butyl methacrylate	1.60– 6.7	7.16×10^{-2}	14,000– 63,000	>0.55	>5,000	No visual separation up to 6.7%. However, 0.7% deduced from tensile and modulus curves	Not apparent up to 63,000

Berlin (155) reported similar behavior for poly(vinyl chloride-*g*-butyl methacrylate) and poly(butyl methacrylate-*g*-vinyl chloride), derived from thermomechanical curves.

Jendrychowska-Bonamour (13), however, reports on anomalous behavior for poly(tetrafluoroethylene-*g*-styrene). The difference in behavior at 20, 90, and 170°C is best illustrated by Figs. 36, 37 and 38.

At 20°C, Teflon recrystallizes under tensions less than 1 kg/mm^2, resulting in a "necking" of the specimen, but grafted with styrene in excess of 19% the recrystallization is blocked by the poly(styrene) branches. At 90°C, above the second-order transition of poly(styrene), elastic deformation of the grafted chains only partially hinders recrystallization. Consequently most samples now show necking, even at smaller stresses. At 140°C (Fig. 38) the poly(styrene) is molten and has a slight lubricating effect. All samples show necking; the high grafting ratios neck at lower values than the pure Teflon.

It would appear that anomalies can occur, even in the best established systems such as poly(ethylene-*g*-styrene). Bachman's (162) and Behr's

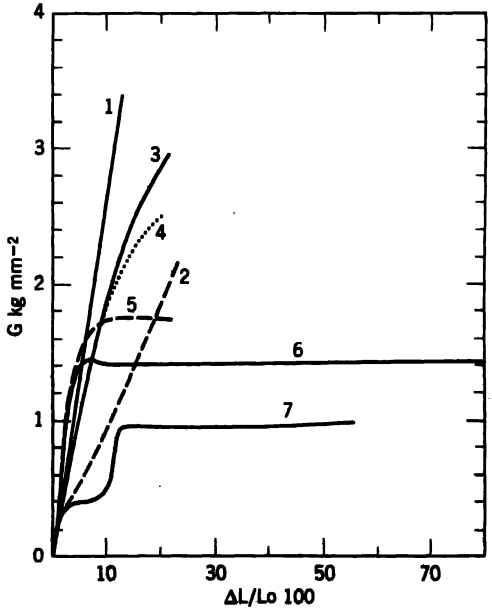


Fig. 36. Stress–strain curve for Teflon films grafted with styrene (at 20°C) (13). Curve (1) 78% poly(styrene); (2) 60%; (3) 44%; (4) 19%; (5) 12%; (6) 7%; (7) Teflon.

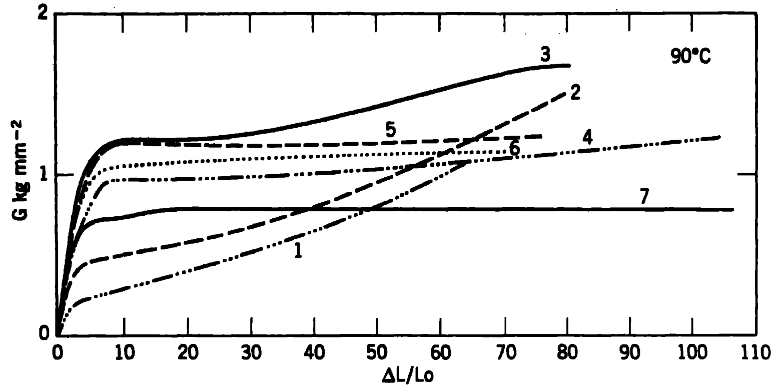


Fig. 37. Stress–strain curves for Teflon film grafted with styrene (90°C) (13). (Code numbers as in Fig. 36.)

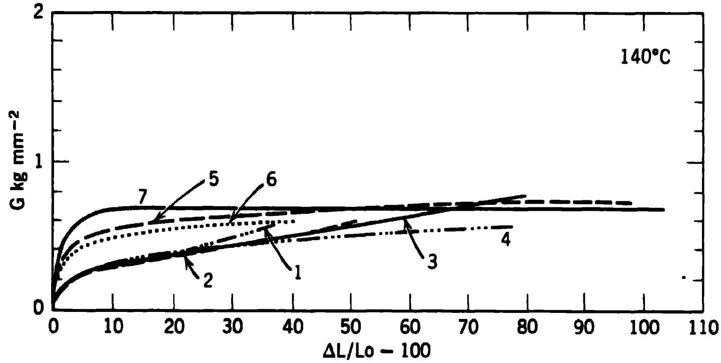


Fig. 38. Stress–strain curves for Teflon films grafted with styrene (140° C) (13). (Code numbers as in Fig. 36.)

(173) results, for example, are directly contradicted by Anderson (172) who prepared such grafts by preirradiation with gamma rays *in vacuo*. His grafts show a definite rise in tensile strength as compared with poly(ethylene) and corresponding blends (Table XI).

A blend of a graft copolymer containing 31% styrene with a blended sample of the same composition gave a tensile value of 1520 ± 30 psi while the strongest blend has a tensile strength of 720 ± 70.

It is known from the school of Kargin (25) that, among the many interesting properties of graft copolymers, is their apparent ability to make

TABLE XI

Properties of Compression Moldings of Grafts and Mixtures

Styrene, wt %	Tensile strength, psi	Elongation, %
	Poly(ethylene)-poly(styrene) blends	
0	1.180 ± 50	30 ± 2
5.0	1.100 ± 10	37 ± 5
15.0	1000 ± 50	5
25.0	630 ± 80	5
35.0	720 ± 70	5
50.0	570 ± 30	5
65.0	690 ± 80	5
	Poly(ethylene)-poly(styrene) graft copolymers	
15.3	1.480 ± 40	32 ± 6
22.5	1.910 ± 90	5
29.6	1.660 ± 30	5
32.9	1.850 ± 10	5
32.9	1.870 ± 30	5
38.2	1.770 ± 20	5
41.5	2.440	5

physical mixtures of dissimilar polymers compatible. Anderson's results may possibly be explained along these lines. Yasuda (174) used the argument of increased compatibility of homopolymers due to the presence of graft copolymer to explain the extreme clarity of grafted cellulose acetate films.

The general rule requiring a reduction of tensile properties with increased grafting must be qualified, therefore, with still another consideration: modified compatibility of homopolymers present due to graft copolymer. Consequently, it would appear that each case should be considered individually and that graft copolymers are capable of producing unexpected properties of some importance.

Good examples were recently provided by Natta (244,245) who developed a series of poly[(ethylene-*co*-propylene)-*g*-vinyl chloride] as impact improvers for PVC. Presumably, the graft improves the compatibility of an otherwise incompatible blend of PVC and ethylene/propylene elastomers. Natta (244) proposed the use of poly[(ethylene-*co*-propylene)-*g*-styrene] as impact improvers for poly(styrene), based on morphological considerations. Gesner (247) and Vasilev (246) also studied the morphology of synthetic and natural rubber graft in the same context.

F. Miscellaneous Properties

Grafts have applications or potential applications other than in bulk form.

1. *Modification of Surfaces*

Surface modification has been described by a number of authors and has been reviewed by Ceresa and others (4).

Job and Lebel (175) recently described the modification of the surface of poly(ethylene) by polyacrylic acid grafts. Their conclusions are in many ways representative of this class of surface treatment. The morphology of the polyacrylate chains grafted on the surface of a solid low density poly(ethylene) was sensitive and determined by its chemical and physical history. The transformation obtained by ionizing and subsequently deionizing the acid groups of the graft chains brought about an irreversible change in conformation. The patent literature on this subject is extensive and has been reviewed in Part II of this volume. It may be of interest to note that the specific irreversible changes in surface structure, at least for surface grafted nylon, was patented (176), and the bulk of information on surface modification of polymer substrates by grafting is contained in the patent literature. Interesting applications, such as the manufacture of ion exchange membranes from paper (Richards, 177), are a direct consequence of surface activity induced in and on the supporting cellulose fiber.

Grafts have also been used for the modification of nonpolymeric surfaces such as clay (Friedlander, 178) and glass fibers. Poly(styrene) was grafted onto glass fibers by Skorynina (179) and Lipatova (180) for the eventual production of superior reinforced plastics. Lipatova (180) grafted three-dimensional epoxide resins onto glass for similar applications. Suzuki (140) and Usmanov (73) grafted rayon tire cord with various vinyl monomers to improve compatibility with rubber.

The application of surface modification by grafting is widely used in the fiber field to change dyeability, weathering, microbiological attack, water sorption. Representative work has been assembled in Tables XII, and XIII, but for details the reader is referred to the appropriate literature; for example, Stannett's (181) review.

The adhesive and wetting properties of poly(ethylene tetrafluoride) can be modified by surface grafts. Seidler (238) investigated acrylic acid grafts; Korshak (232) experimented with styrene and methyl methacrylate grafts; Weiss (234) established some general principles involved. These papers are mainly concerned with the grafting of vinyl monomers. Manaka (233), however, used poly(ethylene tetrafluoride-*g*-methacryl glycidyl ester) to

TABLE XII
Properties of Grafted Fibrous Materials

Author	Ref.[a]	Polymer system	Method of testing	Properties measured
Usmanov et al.	76	Cellulose grafted with acrylonitrile, vinyl acetate, methylvinylpyridine, styrene, alkyl methacrylates	Various	Microbiological action; weathering dyeability; adhesion to rubber
Sakurada et al.	119	Cotton fabric grafted with styrene	Various	Tensile; weatherability; dyeability
Matsuda et al.	118	Cellulose acetate yarn grafted with styrene	Various	Mechanical strength as function of composition
Usmanov et al.	73	Cotton cellulose grafted with acrylonitrile, styrene	Various	Dyeability; adhesion to rubber
Azimov et al.	120	Cellulose grafted with acrylonitrile	Various	Dyeability; water sorption; resistance to microorganisms
Arthur and Blouin	122 123	Cellulose grafted with acrylonitrile, styrene	Various	Modulus; tensile properties
Sakurada et al.	125	Cellulose grafted with styrene	Various	Elastic recovery; thermosetting properties
Kenaga et al.	126	Wood cellulose grafted with vinyl monomers	Various	Tensile properties; abrasion resistance
Kulkarni et al.	134	Cotton (fabric) grafted with acrylonitrile	Various	Microbiological degradation; tensile properties; tear strength
Bergheim et al.	132	Cellulose and paper grafted with vinyl monomers	Various	Tear, burst, tensile strength
Arthur et al.	131	Cotton grafted with acrylonitrile, styrene	Various	Resilience; stiffness; tensile strength; elongation
Vasiliu et al	137	Cotton grafted with acrylonitrile	Various	Thermal, chemical stability
Usmanov et al.	141	Cotton grafted with vinyl monomers	Various	Thermal stability; tensile properties; microbiological degradation; dyeability; water sorption

(continued)

TABLE XII (*continued*)

Author	Ref.[a]	Polymer system	Method of testing	Properties measured
Khakimov et al.	100	Cellulose grafted with vinyl monomers	Various	Water vapor sorption; integral heat of wetting.
Pikler et al.	103	Cellulose grafted with styrene	Various	Thermal stability; tensile properties; cyclic testing
Azizov et al.	148	Cellulose grafted with vinyl monomers	Various	Tensile properties; weatherability
Ide et al.	149	Cellulose acetate grafted with vinyl monomers	Various	Tensile properties
Tsuji et al.	150	Cellulose grafted with styrene	Various	Tensile properties; thermoplasticity; dimensional stability; water repelling
Azizov et al.	151	Cellulose grafted with styrene	Various	Tensile properties; chemical resistance; water sorption; heat of wetting
Gulina et al.	208	Cellulose-*g*-poly(styrene)	–	Improved water and hydrolytic resistance; stability to UV and γ-radiation
Koratkova et al.	207	Cellulose-*g*-poly(methyl vinyl ketone)	–	Improvements in light resistance; thermal stability; wear resistance
Negishi et al.	206	Cellulose grafted with acrylate homologs	–	Dry and wet crease resistance as function of grafting ratio and length of ester group
Usmanov	205	Cellulose-*g*-poly(acrylonitrile)	–	Resistance against bacterial attack as function of grafting mode
Tsuji et al.	204	Cellulose-*g*-poly(butadiene)	–	The following properties were improved: elasticity; heat setting; abrasion resistance; adhesion to rubber
		Cellulose-*g*-poly(butadiene-*co*-styrene)	–	
		Cellulose-*g*-poly(butadiene-*co*-acrylonitrile)	–	

Movsum-Zade et al.	203	Cellulose triacetate-*g*-poly(butylacrylate)	–	Internal plastication
Koratkova	209	Cellulose-*g*-poly(methyl methacrylate) Cellulose-*g*-poly(butyl acrylate)	–	Softener; internal plastication
Movsum-Zade et al.	210	Cellulose-triacetate-*g*-poly(methylmethacrylate)	–	Internal plastication
Walsh et al.	211	Cellulose-*g*-poly(allyl acrylate)	–	Crease recovery of cotton fabrics
Negishi et al.	212	Cellulose-*g*-poly(acrylate homologs)	Tensile, etc.	Crosslinked with formaldehyde, particularly the *n*-butyl ester, shows improved overall properties, compared to ungrafted cotton
Lee and Fuji	213	Cellulose-*g*-poly(methyl methacrylate)	–	Paper pulps of improved properties, effect of graft on pulping rate
Shirakashi	214	Cellulose-*g*-poly(methyl methacrylate)	Dynamic	Effect of grafting ratio and humidity on dynamic modulus and loss

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[a] References arranged in chronological order

TABLE XIII

Properties of Grafted Synthetic Fibers

Author	Ref.[a]	Polymer system	Method of testing	Properties measured
Haas et al.	116	Nylon fibers grafted with ethylene oxide	Various	Tensile properties; permeability to moisture; T_g, T_m
Sakurada and Okada	152	Poly(vinyl alcohol) fibers grafted with styrene	Tensile	Tensile properties; chemical resistance
Odor and Geleji	121	Poly(propylene) yarn grafted with acrylic acid, other vinyl monomers	–	Dyeing properties
Tsuji et al.	124	Poly(propylene) fibers grafted with styrene, etc.	Various	Elasticity; thermoplasticity; tensile strength; thermal, dimensional stability
Sakurada et al.	127	Poly(propylene) fibers grafted with styrene–sulfur dioxide mixtures	Various	Thermal stability; tensile properties
Azimov et al.	120	Natural silk grafted with acrylonitrile	Various	Dyeability; tensile properties
Shinohara	128	Nylon fibers grafted with vinyl monomers	Various	Tensile properties, moisture region dyeability; thermal properties
Shinohara and Mukoyama	130	Polyolefin fibers grafted with vinyl monomers	Various	Tensile strength; torsional rigidity; Young's modulus; dyeability
Matsuda et al.	138	Synthetic fibers grafted with vinyl monomers	Thermo-mechanical	Tensile properties; thermal stability
Stamm et al.	136	Poly(propylene) fibers grafted with chloromethylstyrene	–	Tensile properties; dyeability; moisture regain
Wu et al.	142	Poly(propylene) fibers grafted with acrylic acid, acrylonitrile, vinylpyridine	–	Tensile properties
Korshak et al.	135	Poly(-ε-caproamide) grafted with acrylic acid and heavy metal salts	–	Tensile properties
Armstrong and Rutherford	88	Various fibers grafted with vinyl monomers	–	Water sorption; tensile properties; Youngs's modulus

Tutaeva et al.	109	Viscose fibers grafted with bis(triethylene glycol) phthalate dimethacrylate	Various	Tensile properties
Torikai et al.	143	Poly(propylene) fiber grafted with vinyl acetate	–	Mechanical, thermal properties; dyeability; resiliency
Gnip et al.	144	Polyamide fiber grafted with acrylonitrile, UV light and vinyl acetate	UV light	Tensile properties as function of light stability and grafting ratio
Robalewski et al.	139	Polyolefin fibers grafted with vinyl monomers	–	Tensile properties; thermal stability; dimensional stability
Suzuki et al.	140	Rayon grafted with vinyl monomers	–	Tensile properties
Wu et al.	142	Poly(propylene) fibers grafted with acrylonitrile	–	T_m; T_g; tenacity, elasticity
Tutaeva et al.	146	Viscose fibers grafted with polyester acrylate	–	Tensile properties
Tutaeva et al.	147	Viscose fibers grafted with linear and three-dimensional polymers	–	Tensile properties
Movsum-Zade	145	Cellulose triacetate grafted with methyl methacrylate	–	Tensile properties, T_g
Zielinski and Achmatowicz	226	Poly(ethylene terephthalate-*g*-4-vinylpyridine)	–	Dyeing properties investigated
Kurilenko et al.	227	Kapron-*g*-poly(styrene)	Tensile	Kapron grafts decrease in strength when grafted Lavsan increases; difference explained
		Lavsan-*g*-poly(styrene)	–	
Geleji et al.	228	Poly(propylene-*g*-methyl methacrylate)	Tensile	Effect on tensile properties, dye uptake investigated
		Poly(propylene-*g*-styrene)	–	
		Poly(propylene-*g*-caprolactam)		
Sakurada	229	Poly(vinyl alcohol-*g*-styrene)	Tensile	Mechanical properties, water uptake studied as function of grafting ratio
Pavlinec et al.	230	Poly(propylene-*g*-glycol methacrylate)	–	Improvement in dye uptake; swelling of fiber increased

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[a] References arranged in chronological order.

obtain a surface with reactive epoxy groups for chemical bonding. Similar work was carried out by Friese (235) and Manaka (233) for poly(ethylene). Lewis (231) investigated the adhesion to metals of poly(propylene) grafted with a large number of phosphor- and boron-containing vinyl derivatives.

Another aspect is the surface modification by grafting of nonpolymeric surfaces such as carbon black (Ohkita, 236) and silica (Runge, 237). This type of modification is of industrial importance, but is outside the scope of this book.

2. Permeability

The permeability of graft and block copolymer films to gases and vapors depends upon both the composition and the structure of the copolymer. For example, Haas (116) found that moisture permeability of polyamides grafted with ethylene oxide increased with the degree of grafting. The opposite is true for nylon grafted with styrene (Dasgupta, 182). Myers (160) found that poly(ethylene) film grafted with acrylonitrile had a reduced gas permeability. It was postulated that the grafted poly(acrylonitrile) acts as a low permeability filler within the poly(ethylene) amorphous regions. Myers contrasted this behavior with similar styrene grafts. Here a minimum in permeability with graft content occurred. The increased permeability at high grafting ratios was attributed to the destruction of crystallite regions.

3. Dielectric and Other Properties

Dielectric properties can be changed by grafting. Poly(1-butene-*g*-styrene), for example, prepared by Pegoraro (183) exhibits a higher dielectric constant and loss factor than either of the homopolymers. Ion exchange membranes have been made by sulfonating styrene grafted on poly(ethylene) (Mesrobian, 166; Chen, 184). Similarly, ion exchange properties were obtained by quaternizing vinylpyridine grafted to poly(ethylene) (184) or acrylic acid to paper (177).

Sykes (185) modified the surface resistivity of nylon, and Houlton (186) lowered static properties of polyester fibers by quaternizing poly(vinylpyridine) grafts on these fibers.

Chen (184) improved the solvent resistance of silicon rubbers by grafting with acrylonitrile. The dyeability and adhesion of polyolefin fibers and films were studied by Houlton (186), Levine (187), Sykes (185), and Shinohara (188).

Electrical conductivity during or caused by radiation may be reduced by grafting (Yagahe, 241). High electrical conductivity and ion exchange properties can be obtained, according to Kuznetsova (242), by grafting poly(ethylene) with 2-methyl-5-vinylpryidine, acrylic and methacrylic acid. Tevlina (243) achieved similar results with phosphorylated poly(ethylene-*g*-styrene).

G. Grafts of Fibrous Materials

Many of the properties discussed for bulk graft copolymers apply equally as well to fibrous materials. It is not our intention to deal with this area of graft copolymers exhaustively. Atlas and Mark (224) and Schwarz and Roudiex (225) recently published reviews, the latter dealing mainly with radiation grafting. It was felt, however, that some attention should be paid to the similarities and dissimilarities between bulk and fiber grafts. For example, grafting on drawn or undrawn species of the same fiber has a large influence on the physical properties of the resulting fiber. Shinohara (189), Magat (190), and others remarked on effects on the crystalline structure of nylon fibers due to grafting with acrylic acid and maleic acid. Except where only surface modification was intended, grafting has little influence on the tensile properties of the fiber, as long as the integrity of the structure is preserved. In Table XII, a cross section of the literature relating to grafting on cellulose substrates has been presented.

Most workers quoted agree that, at least in the case of cellulose, tensile properties are not affected, or decrease with high grafting ratios. This decrease is sometimes due to secondary effects of the grafting operation. Usmanov (106) recently reiterated this opinion. Grafting on cellulose is, therefore, mainly useful to alter other properties, such as resiliency, stiffness, thermal stability, chemical stability, thermosetting properties, dyeability, water sorption, weatherability, adhesion, resistance against microbiological attack, and wetting. Iwakura (191) prepared chemically reactive cellulose fibers by grafting with glycidylmethacrylate. These fibers can then be reacted chemically with dyes, or given ion exchange properties.

Much of what has been said about cellulose grafts applies to synthetic fibers as well. Again a cross section of the literature has been compiled in Table XIII, without being exhaustive. If the structure of the fiber is not destroyed, tensile properties stay the same or show a decrease, with increasing grafting ratio. In the synthetic field, a greater likelihood exists that drastic changes do occur and consequently obvious improvements achieved in secondary properties are usually accompanied by a sacrifice of tensile strength. Korshak (192) confirmed this opinion in a recent review. The effect of microstructure on grafting of poly(propylene) fibers was reviewed by Geleji (193) who also noted the effect of the subsequent disturbance of this structure on physical properties. Negishi (194), however, posed a different opinion and demonstrated that the tenacity of poly(vinyl alcohol) fibers could be improved by grafting.

It is obvious from this short resume that graft copolymers have a distinct and important function to fulfil in the field of fibers.

Some recent work on wool should receive mention. Grafting on wool, seeking shrink resistance and resistance to matting and other desirable properties, has as yet not been fully evaluated. The location of the grafts seems to be of extreme importance and the success of the graft, whether it is by interfacial polymerization (Whitfield, 198), radiation grafting (Stannett, 199), or redox systems (Negishi, 195), is structure-sensitive. Andrews (197) postulated, for example, that acrylonitrile grafted in the keratinous regions of the fiber. Stannett (199) emphasized the importance of the swelling agent used and Whitfield (198) used free amino groups on the surface of the fiber to achieve desirable results. Tokar (196) discussed the properties of 50/50 wool viscose fibers with various acrylic grafts.

The general field of cellulose grafts and their properties has recently been reviewed by Livshits (200), Krassig (201), and Rogovin (202), indicating that a renewed interest has arisen, the structure of cellulose grafts and the effect of cellulose structure on grafting receiving the bulk of attention. Electron micrography was used to elucidate structural effects in cellulose grafts (215,216). Special staining techniques for this purpose were developed by Belavtseva (217). Shirakasai (218), Hsing-Mao Chou (219), and Ho (220) used x-ray analysis to determine configurational changes and fine structure in fiber grafts. Balabaeva (221,223) and Zhbankov (222) used infrared spectroscopy for similar purposes on cellulose grafts.

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V. COMMERCIAL EXPLOITATION OF BLOCK AND GRAFT COPOLYMERS*

From the vast quantity of theoretical work on block and graft copolymers that has been reviewed in this volume, it cannot be denied that this type of copolymer structure has ample potential for commercial exploitation. The most striking fact evident from an examination of this field, however, is the general lack of commercial development. Some hundreds of block and graft copolymer compositions, their properties and methods of synthesis, have been reported in the general literature and, while it is true that the majority of this work has been carried out at academic level, Part II of this volume, which reviews the patent literature, indicates an extremely active industrial interest. During the past decade or so, over 900 patents have been filed by some 150 different companies dealing with graft copolymers alone. Improvements in the dyeing and printing of synthetic fibers, improvements in the film-forming properties of polymers, increased strength, abrasion and crease resistance of cellulose derivatives, impact improvers for thermoplastics, and improvements in the properties of natural rubber are but a few of the many processes and uses of graft copolymers that have been claimed in the patent literature. The most striking fact is that very few of these processes have reached commercial development. The reasons for this will be dealt with later in this section but first let us examine the products at present being marketed which are known to be, or contain, block or graft copolymers.

1. NONIONIC SURFACE ACTIVE AGENTS

The first commercial utilization of the particular properties obtainable from block or grafted polymer structures was the introduction by Wyandotte Chemical Corporation of a series of nonionic surface active agents known as the Pluronics.

The Pluronic polyols are a series of nonionic surfactants prepared by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. This series may be represented empirically by the formula

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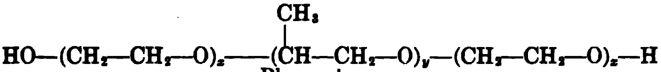
* References for this section will be found on page 239.

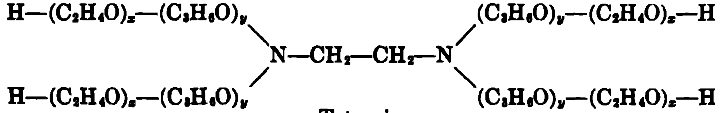


$$HO{-}(CH_2{-}CH_2{-}O)_x{-}(\overset{CH_3}{\overset{|}{C}}H{-}CH_2{-}O)_y{-}(CH_2{-}CH_2{-}O)_z{-}H$$

Pluronics

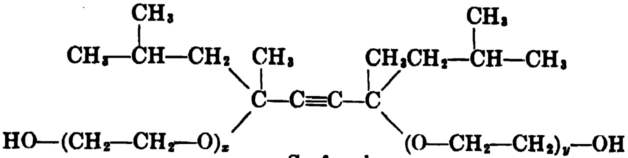
The molecular weight of either the hydrophobic base or the hydrophilic portion can be varied in small increments over a wide range. It is therefore possible to prepare a product to meet many requirements of molecular weight or of hydrophobic–hydrophilic balance. At the present time the following Pluronic grades are available from Wyandotte; L44, L61, L62, L64, F68, P75, L81, P84, F88, P94, F98, L101, P104, and F108. These products cover a wide range of hydrophobic–hydrophilic composition which enable their use in a wide field of applications including cosmetics, plasticizers, pharmaceuticals, paints, water treatment, and formulated detergents. The Pluronics are identified by a letter (L, P, or F) and a two-or three-digit number. The letter identifies the physical form of the particular Pluronic: L for liquid, P for paste, F for flake. The first one or two digits identifies the arbitrary molecular weight range of the hydrophobic base while the second or third digit (multiplied by a factor of 10) gives the approximate percentage of ethylene oxide in the total molecule. The Pluronics exemplify the almost theoretical concept of block and graft copolymers—the possibility of tailor-making a polymer with desired physical and chemical characteristics.

The Tetronics, another series of nonionic detergents marketed by the Wyandotte Chemical Corporation, are prepared by initiating the ring opening of the propylene oxide molecule with ethylene diamine. The tetrabranched poly(propylene oxide) so formed is then used to initiate the block copolymerization of ethylene oxide (1). The structure of the product may be visualized as shown. The general characteristics of the Pluronics and Tetronics and the effects of segment length on detergent properties have been described by Vaughn, Jackson, and Lundsted (2).



Tetronics

Another series of nonionic surfactants known as the Surfynols are marketed by the Air Reduction Chemical and Carbide Co. These products are obtained by the combination of tetramethyldecynediol with two chains of ethylene oxide. Two grades of Surfynols are at present being marketed; grade 104 (2,4,7,9-tetramethyl-5-decyne, 4,7-diol) and grade TG, which is Surfynol 104 with an alkyl phenyl ether of poly(ethylene glycol) in ethylene glycol added.



Surfynols

2. CELLULOSE GRAFTS

A. Vinyl Acetate Grafted Cellulose Acetate

Talet (3) has reported the grafting of up to 700% vinyl acetate onto cellulose acetate. The resulting product retained a softening point in excess of 100°C even when a small fraction of difunctional monomer was added to the polymer-monomer mixture. The polymer was easily moldable, presented good mechanical properties, and was able to withstand prolonged contact with boiling water. According to Chapiro (4), fabrication of this material was commenced on a pilot-plant scale in 1957 by Societe Nobel-Bozel using γ rays from an 800 curie Co^{60} source to initiate grafting but since then no further details have been found in the literature.

B. Ethylose

The Rayonier Company has reported (5) the production of a cellulose graft material known as Ethylose, a wood cellulose modified with ethylene oxide. The structure of the product is reported to have one ethylene oxide unit for each 20 cellulose units in the chain. Rayonier claim that they can produce 3000 tons of Ethylose per year and that they will sell the material for 50¢ a pound. Potential markets include coated papers, textiles, ceramics, and foodstuffs.

3. HIGH IMPACT POLY(STYRENE)

Poly(styrene) with improved impact properties can be prepared by polymerizing styrene in the presence of about 5% of a butadiene–styrene rubber. The final product is a mixture of homopolymers and a certain amount of grafted material. Physical blends of poly(styrene) and styrene–butadiene rubber are also available commercially but they have a lower impact strength than equivalent rubber–styrene polymerized products. The difference is usually explained as being due to graft copolymer providing a measure of compatibility and, therefore, adhesion between the rubber and poly(styrene) phases. Thomas (6) has suggested, however, that the role of grafting may be overemphasized and that the merit of copolymerized product over a physical blend is possibly associated with a particular distribution of phases in the former.

The Macromol Corporation of Passaic, N. J. market various grades of poly(styrene)–rubber grafts under the trade name of Macrolene (7). Macrolene 555, 5515, 6415, and 7315 are high impact polymers and Macrolene 1037, 1046, 1055, 461, and 4615 are the medium impact grades.

Aquitaine Plastique of Paris also market a series of high impact poly(styrenes) called the Lacquenes (8). Lacquenes 500, 625, 650, 800, and 825 are the grades presently available.

The Solar Chemical Corporation of Leominster, Mass. have recently announced (9) the development of five new grades of graft modified high impact poly(styrenes) for injection molding and extrusion. The tensile strengths range from 3800 to 5500 psi and elongations are quoted ranging from 5–10% for the 220G grade up to 35% for the 1200G grade. The resins are available in 1/8 in. and 1/16 in. pellets, with or without external lubrication.

4. NATURAL RUBBER GRAFTS

The polymerization of methyl methacrylate in a natural rubber latex medium gives rise to a mixture containing graft material and a substantial proportion of unmodified homopolymers. The products show a well defined dual nature which might be expected of a graft copolymer. A hard form predominantly reflecting the properties of the plastic components and a soft rubbery form possessing quite different properties can be isolated from the same product (10). The configurational differences in these two forms even survive ordinary curing processes to give stiff and soft vulcanisates.

The natural rubber–methyl methacrylate grafts were developed by the British Rubber Producers Research Association and are marketed as Hevea plus MG. The best known product is called Hevea Plus MG 50, and contains 50% methyl methacrylate. It combines the hardness and rigidity of the thermoplastic component with the high impact resistance of rubber. Conventional cure is required to realize maximum strength properties and filler or plasticizer can be added to harden or soften the compound. Normal rubber equipment can be used for press molding, and injection molding can be done by suitably increasing the hardness with reinforcing filler. Another grade containing 40% methyl methacrylate is recommended for adhesive applications (6). The Hevea Plus MGI latices are also graft copolymer mixtures but these are prepared by a radiation method. Although of similar composition, the colloidal and film-forming properties of MGI rubber latices show striking differences from those of equivalent MG latices. This phenomenon has been discussed earlier (see p. 66). The SG series of Heveaplus are also available commercially. The polymers differ from the MG series in that styrene replaces the methyl methacrylate. The United States Rubber Company market a similar product known as SM latex (11).

5. ACRYLONITRILE-BUTADIENE-STYRENE POLYMERS

Acrylonitrile-butadiene-styrene terpolymers (ABS) are thermoplastic polymers produced either by blending styrene-acrylonitrile copolymer resins with butadiene-based elastomers, or by grafting styrene and acrylonitrile onto poly(butadiene). Although they could be classified as a special kind of high impact polystyrene, ABS polymers are generally considered as a separate class. They exhibit an extraordinarily desirable combination of mechanical, thermal, chemical, and electrical properties, as well as ease of processing and a moderate price. As engineering plastics, the ABS polymers can be classified with nylon resins, acetal resins, and polycarbonates. They are used when performance along with relatively low cost is desirable; typical applications are in telephones, pipes, household appliances, automobile parts, luggage, shoe heels, and packaging.

Up to 1960, two companies, United States Rubber's Naugatuck Chemical Division and Borg-Warner's Marbon Chemical Division, were the sole producers of ABS, selling the material under the trade names Royalite, Kralastic, and Cycolac. Two other companies, B. F. Goodrich and Monsanto Chemicals, selling their products under the names Abson and Lustran, respectively, have now entered the field, and Marbon has added further types known as Cycolon and Blendex. Other companies are also showing interest. Union Carbide, Foster Grant, Dow Chemical, Canada Polymer, Celanese, Firestone, International Latex, and United Carbon are all reported to be actively engaged in the ABS field and products from these firms are gradually reaching the world market (12). Few companies disclose their manufacturing process and it is often not clear which of the grades marketed are blends or actual graft copolymers. Novodur PM and Cycolac T manufactured by Farbenfabriken-Bayer, and Borg-Warner, respectively, are known, however, to be graft products of the general formula poly[butadiene-*g*-(styrene-*co*-acrylonitrile)]. Both these products contain about 30% poly(butadiene) and 70% styrene-acrylonitrile copolymer in the ratio 70–75:30–25. The mechanical and electrical properties of the Novodur PM graft product and the Novodur blends HG and W and the way in which these properties suit them for various applications, have been described by Ebneth (13).

6. WOOL GRAFTS WITH IMPROVED PROPERTIES

Increasing popularity of synthetic fibers in the textile industry has led to increased research effort into improving the properties of wool. A significant advance in solving the problem of shrinkage and "pilling" (the formation of unsightly balls of fiber on the surface of woolen fibers), has recently been announced by the U.S. Department of Agriculture's Wool and Mohair Laboratory, Albany, California (15). Using the interfacial polymerization technique (see Chapter III), nylon 610 is chemically grafted onto and surrounding each wool fiber. The treated wool contains less than 1% nylon but it can be safely machine-washed and tumble-dried without danger of shrinkage.

The wool grafting treatment is essentially easy to apply and is relatively cheap. The process known as Wurlan consists of passing the fabric through a 1% aqueous solution of hexamethylenediamine containing an inorganic base and a nonionic wetting agent. The fabric is then squeezed to remove excess liquid and then passed through a 2–3% solution of sebacoyl chloride in a hydrocarbon solvent. After further squeezing the fabric is washed and dried. The treatment of wool by this technique is now well established. Several million yards of treated wool was produced in the United States in 1965 and the application is reported to be rapidly increasing.

The major problem hampering the commercial development of graft copolymers is the presence of homopolymer which invariably forms during synthesis. Although methods of synthesizing graft copolymers with little or no homopolymer have been developed (see, for example, Chapter III) these processes are generally very inefficient and yield only small amounts of product. They are not, in general, economically feasible. Unless an efficient and economic process or a simple and inexpensive method of homopolymer separation can be devised, the development of graft copolymers will be restricted to systems in which the presence of homopolymer is not detrimental to the properties of the grafted structure. This, of course, limits the field rather severely. It is almost certain, however, that graft copolymers will continue to be of importance as impact improvers, especially for high impact poly(vinyl chloride), poly(propylene), and the poly(acrylates).

Block copolymer synthesis does not in general suffer from the limitations of homopolymer contamination encountered in grafting. In some ways this makes the use of block-type structures more attractive for commercial development. Indeed, one of the most encouraging developments to be reported lately (6) is in the field of the crystalline block copolymers of α-olefins prepared using Ziegler type catalysts (14). Advantage is taken of the fact that ion pair complexes which permit chain propagation have long active lifetimes. A Ziegler catalyst is used to build up a long stereoregular chain of units of one monomer and a second monomer is then added so that it polymerizes onto the end of the still active polymer chain to give a linked segment of a second component. Crystalline block copolymer is thus produced by alternating the feeds of two or more monomers. Eastman Chemical Products have recently released sample quantities of crystalline ethylene-propylene polymers known as "poly(allomers)" and it is believed that these are in fact prepared by a Ziegler–block copolymerization process. These polymers exhibit properties which are a composite of the general properties of poly(propylene) and high density poly(ethylene). The poly(allomers) appear to be the first commercial examples of block copolymers produced from unsaturated addition-type monomers and their properties indicate that this may be a fruitful field for further commercial development.

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PART II

PATENT LITERATURE

VI. GENERAL COMMENTS ON THE PATENT LITERATURE

The patent literature on graft copolymers and graft copolymerization has been abstracted and is presented in the following appendixes. The abstracts have been compiled from information available from *Chemical Abstracts* and the Library Services Section of Imperial Chemical Industries Plastics Division whose valuable assistance the authors gratefully acknowledge. The search cannot be claimed to be completely exhaustive due to obvious physical and geographic limitations; notwithstanding this, however, 902 patents have been found in a search terminated on April 30, 1966. This date applies to the journals and other sources available and not to the actual publication date. The information has been presented in the following manner.

Appendix I contains a key index relating patent number to the reference number of the relevant abstract. The information is arranged according to country of origin.

Appendix II lists, in order of application date, abstracts of 902 patents pertaining to graft copolymers and graft polymerization. Unfortunately, a number of patents were located for which the application date was not readily available. These have been recorded in order of publication date in Appendix III.

Statistics on companies holding patents in the field reviewed are contained in Appendixes IV and V.

Two major classifications have been attempted according to the method of grafting employed and the polymer composition claimed. The first classification is based on an analysis supplied in Part I of this volume and, where available, a reference to the first publication of the method employed in either the general or patent literature has been supplied.

In many cases the full patent specification was not readily available and it was therefore not always possible to determine the exact polymers claimed. To overcome this problem the alphabetical index of graft copolymers has been divided into three parts containing, respectively, specific polymers, polymers containing either a backbone or grafted side chain of uncertain composition, and a list of patents with claims of such a general nature that indexing was impossible.

Of the 902 patents abstracted, 728 represent parent patents and 174 equivalents or near-equivalents filed in other countries. Methods of synthesis utilizing ionizing radiation are covered by 224 patents, representing 24.8% of the total. These in turn are composed of 157 main patents and 69 equivalents.

There is a total of 152 patentees of which 75 have one patent and 23 have 10 or more. Farben-Fabriken Bayer and Farbwerke-Hoechst appear to be the most active participants in the field at present although United

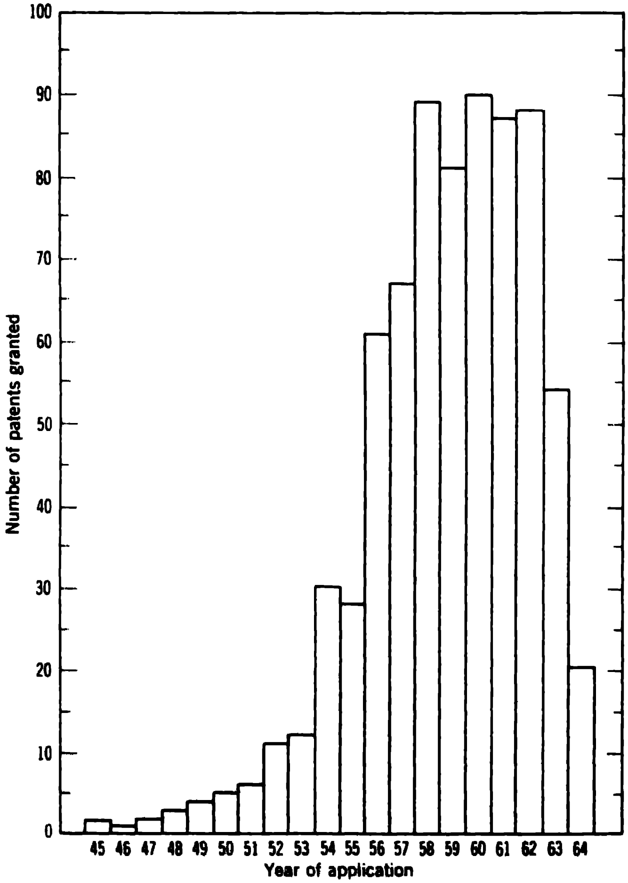


Fig. 39. Number of graft copolymer patents applied for per year.

States Rubber, the Japanese Toyo Spinning Company, and the USSR have shown increased activity. Dow and Du Pont indicate a maximum in patent activity from 1957 to 1959 with the publication of 55 and 18 patents per company, respectively. This activity appears to have tapered off in the last five years, although, with 113 graft patents between them, Dow and Du Pont are still by far the leaders in the field. ICI and Esso, on the other hand, have a rather steady patent output, each company publishing on the average one graft copolymer patent per year. Further indications of the company patent situation can be obtained from Appendix V.

A majority of the patents published recently deal with butadiene-styrene/styrene acrylonitrile grafts especially as impact-resistant additives for the chlorinated vinyl polymers. The modification of cellulose by grafting also quite popular at present as is evident from the more recent Japanese and Russian publications.

Plotting the number of patents against the year of application gives the graph in Fig. 39 which shows a near exponential increase from 1945 to 1958, a steady period from 1958 to 1962 followed by a sharp drop in the numbers appearing over the last few years. This decline may well be artificial due to the delay in abstraction and publication of patent applications and it is expected that the number of applications will continue to rise. It is interesting to note that while Fig. 39 shows a maximum for general graft copolymer patent applications around 1958–60, applications concerning radiation methods were at a maximum in 1956. In this year radiation methods comprise 40% of the total applications, compared with 25% over the whole period covered by the survey.

APPENDIX I

Patent numbers referring to graft copolymerization and graft copolymers in general are arranged in numerical order and grouped according to country of origin. The column marked "Ref." refers to a short abstract of the patent which is presented in Appendixes II and III.

A list of the actual number of patents filed in each country is also included.

British

Patent No.	Ref.	Patent No.	Ref.	Patent No.	Ref.
507,323	885	788,651	44	825,882	127
604,708	3	791,453	58	828,895	88
624,079	4	791,765	99	829,512	230
652,401	9	801,479	156	830,785	119
667,291	11	801,528	102	831,833	177
675,489	12	801,531	108	832,193	115
715,194	20	806,582	169	832,567	154
718,137	28	809,838	95	832,692	110
733,093	35	814,393	69	832,693	206
742,900	45	816,024	139	833,585	179
749,494	42	816,579	78	834,523	146
750,923	33	817,684	114	834,557	901
757,523	50	819,049	132	834,954	237
766,528	59	819,651	87	837,334	293
766,585	66	820,089	136	837,335	294
766,686	100	820,120	93	838,413	94
767,642	57	820,930	76	839,069	274
771,926	63	821,000	176	839,483	157
778,102	91	821,971	148	840,070	247
778,265	62	822,751	213	840,153	321
779,557	75	823,462	161	841,744	272
786,142		824,263	120	841,889	150
(addn. to	98	824,368	222	842,841	334
766,528)		824,920	121	843,190	134
788,175	89	825,680	194	844,141	384

(continued)

British (*continued*)

Patent No.	Ref.
844,331	355
844,791	287
845,052	369
845,690	267
847,602	242
847,603	245
849,063	320
850,446	284
850,471	153
851,059	141
851,647	311
852,042	162
853,970 (addn. to 809,838)	170
853,971	173
855,711	125
855,720	361
856,329 (addn. to 801,531)	197
856,884	184
858,747	415
858,776	241
860,244	256
860,327	362
860,408	159
861,454	288
861,455	289
861,948	429
862,610	228
863,211	232
863,395	417
865,263	450
865,378	182
866,069	128
866,131	201
866,537	202
866,667	445
867,822	571
869,180	224
869,482	397
869,501	453
870,052	229
871,192	371
871,572	279
872,132	475
872,513	164
872,514	165
872,515	430
872,432	330
872,532	424
874,067	483
875,131	187
875,758	234
876,001	341
876,535	420
879,195	499
881,374	340
883,473	278
883,728	299
883,791 (addn. to 79,1453)	216
883,792	217
883,793	218
884,732	264
887,425	480
887,887	538
888,231	270
890,145	391
890,267	501
891,758	529
891,944	398
892,133	395
892,189	352
894,395	302
894,753	454
894,853	323
895,478	471
896,456 (addn. to 849,063)	504
897,341	548
897,705	409
898,709	297
898,710	304
899,029	553
899,567	528
899,683	402
899,993	533
899,999	325
901,038	305
901,039	307
901,042	346
901,646	367
901,736	351
901,997	282
903,566	561
903,715	385
904,262	498
905,043	356
905,465	347
905,624	575
908,224	488
910,702	328
912,280	404
913,370	559
916,217	375
916,245	358
916,529	551
917,498	406
917,499	407
920,867	616
922,461	473
924,873	456
926,142	463
926,477	381
926,478	382
927,519	583
927,821	464

(*continued*)

British (*continued*)

Patent No.	Ref.	Patent No.	Ref.	Patent No.	Ref.
927,968	604	961,797	704	990,194	679
929,245	545	961,940	496	991,315	664
932,852	586	962,028	708	991,316	688
934,038	405	962,575	564	991,422	657
935,013	477	963,437	661	992,503	681
935,996	423	963,771	655	993,413	588
937,747	468	964,977	536	993,434	648
938,766	640	965,627	716	994,342	595
940,139	626	965,851	703	994,924	788
940,200	465	965,866	725	996,090	824
941,064	447	967,288	753	997,093	610
941,689	636	967,332	522	997,674	778
942,971	668	968,578	750	998,979	721
946,065	589	971,607	701	999,100	602
946,071	432	971,778	611	1,000,082	666
946,404	455	972,229	773	1,001,331	818
946,663	470	973,567	540	1,001,437	833
947,800	619	975,421	550	1,001,953	746
948,747	585	979,652	757	1,002,456	828
950,315	457	980,258	601	1,007,884	845
951,128	685	981,049	735	1,009,109	693
951,274	609	981,584	737	1,013,393	808
952,639	516	982,918	751	1,014,019	848
954,041	608	983,587	570	1,015,236	860
955,258	490	983,817	777	1,015,304	781
956,556	491	985,755	633	1,017,533	686
957,753	627	987,353	741	1,017,861	758
960,192	660	988,516	634		

United States

Patent No.	Ref.	Patent No.	Ref.	Patent No.	Ref.
2,388,685	1	2,569,470	16	2,646,418	23
2,422,550	2	2,602,079	10	2,649,434	
2,524,045	5	2,607,761	8	(ext. of	15
2,527,495	7	2,618,621	13	2,620,324)	
2,542,771	6	2,620,324	18	2,649,435	26
2,556,158	14	2,628,220	24	2,657,191	19

(continued)

United States (*continued*)

Patent No.	Ref.	Patent No.	Ref.	Patent No.	Ref.
2,694,692	17	2,907,675	106	3,029,220	316
2,703,284	22	2,908,657	74	3,029,221	387
2,719,138	27	2,908,661	226	3,030,326	485
2,731,439	34	2,908,662	227	3,035,008	486
2,732,363	30	2,913,426	235	3,035,009	317
2,735,830	31	2,921,044	81	3,035,010	339
2,735,831	32	2,926,126	124	3,036,032	318
2,741,650	25	2,927,093	271	3,036,033	319
2,755,270	36	2,927,095	273	3,038,876	336
2,763,631	29	2,947,718	70	3,044,972	452
2,780,605	46	2,947,719	71	3,046,078	357
2,798,061	111	2,949,436	158	3,047,534	508
2,802,808	47	2,955,015	265	3,048,561	342
2,802,809	52	2,956,899	195	3,049,507	343
2,806,842	113	2,959,569	168	3,049,508	344
2,837,496	37	2,965,571	257	3,050,498	345
2,838,470	54	2,965,572	258	3,057,816	541
2,839,491	39	2,970,129	209	3,057,817	542
2,840,447	61	2,972,593	117	3,058,950	435
2,841,569	68	2,979,447	388	3,061,531	649
2,842,518	72	2,984,608	359	3,062,777	40
2,842,519	73	2,987,501	419	3,065,041	366
2,843,561	92	2,989,420	422	3,066,085	290
2,843,562	151	2,990,393	392	3,067,163	380
2,849,419	60	2,996,469	376	3,068,122	354
2,850,479	109	2,996,470	377	3,068,187	497
2,857,360	118	2,998,329	276	3,068,764	500
2,859,201	51	3,008,885	364	3,069,382	208
2,861,974	129	3,010,936	394	3,070,573	396
2,862,906	248	3,012,000	155	3,070,574	365
2,862,907	249	3,014,008	383	3,072,599	506
2,865,872	77	3,019,208	53	3,072,600	507
2,867,601	85	3,020,257	349	3,073,798	518
2,873,240	178	3,022,264	337	3,074,906	467
2,879,253	55	3,022,265	338	3,075,857	372
2,879,254		3,026,289	82	3,075,948	513
2,882,290	67	3,026,292	434	3,079,295	478
2,883,360	56	3,026,293	494	3,081,242	281
2,891,018	101	3,027,346	210	3,082,186	514
2,899,405	80	3,028,359	466	3,083,172	446
2,901,458	86	3,029,218	314	3,083,176	509
2,905,653	261	3,029,219	315	3,083,177	510

(continued)

United States (*continued*)

Patent No.	Ref.	Patent No.	Ref.	Patent No.	Ref.
3,083,178	511	3,107,207	312	3,143,521	582
3,083,179	512	3,110,695	578	3,143,522	675
3,084,138	515	3,111,370	736	3,144,420	713
3,086,959	502	3,111,424	107	3,144,426	549
3,087,875	373	3,111,501	428	3,148,020	654
3,088,791	439	3,118,854	443	3,157,460	621
3,090,664	360	3,119,785	469	3,162,695	680
3,090,766	436	3,119,786	547	3,162,697	659
3,092,512	414	3,121,672	291	3,167,598	714
3,093,615	332	3,123,434	123	3,170,892	566
3,094,504	503	3,130,076	697	3,170,964	687
3,094,505	505	3,130,177	656	3,177,268	663
3,095,401	492	3,131,163	672	3,177,269	605
3,097,185	393	3,133,041	437	3,177,270	606
3,097,186	543	3,133,825	581	3,179,485	544
3,098,838	523	3,134,746 (continuation of 3,017,391)	678	3,180,908	594
3,099,631	353			3,183,056	709
3,100,757	482			3,185,659	631
3,100,758	525			3,187,067	580
3,101,275	262	3,136,738	539	3,192,178	629
3,101,276	266	3,137,674	625	3,196,124	738
3,106,482	637	3,141,862	650	3,222,323	760
3,107,206	286				

Belgian

Patent No.	Ref.	Patent No.	Ref.	Patent No.	Ref.
547,078	96	559,514	171	569,890	275
547,688	103	559,515	174	570,822	285
553,374	191	560,986	185	571,542	411
555,759	133	561,742	196	572,100	298
556,134	137	562,397	212	572,125	296
556,633	140	562,661	220	572,577	306
556,649	145	564,910	233	572,578	303
556,974	147	565,853	244	572,579	309
558,004	152	566,903	255	572,906	310
558,898 (addn. to 546,815)	166	568,423	292	573,388	322
		569,421	268	574,580	331
		569,852	277	575,094	335

(*continued*)

Belgian *(continued)*

Patent No.	Ref.	Patent No.	Ref.	Patent No.	Ref.
575,430	390	629,203	729	643,168	815
577,722	378	630,088	734	643,626	820
578,271	418	630,843	745	643,940	826
578,864	379	631,408	749	644,936	827
581,798	401	632,249	747	646,258	834
583,429	413	633,903	756	646,284	830
585,104	425	634,284	761	646,285	831
586,455	532	634,545		648,686	
596,692	569	(addn. to	765	(addn. to	840
603,086	562	609,158)		619,525)	
605,139	572	634,955	766	649,464	882
605,552	574	635,024	774	652,054	854
606,944	587	635,415	767	652,069	850
607,015	590	636,312	789	652,120	
607,122	596	636,450	772	(addn. to	852
607,269	597	636,696	791	636,977)	
612,235	632	636,977	775	652,191	851
613,991	647	636,997	776	657,762	864
615,768	658	638,208	785	659,430	867
617,057	665	638,209	786	660,860	871
617,230	669	638,556	787	663,290	873
617,260	670	638,939	809	663,603	875
618,194	752	639,890	797	663,786	874
623,166	698	640,039	795	663,931	
625,434	710	641,598	802	(addn. to	876
625,479	644	641,599	804	636,977)	
626,518	806	641,842	836	664,090	880
627,414	724	641,883	810	665,220	879
628,348	726	641,894	807	665,479	881
629,046	727	642,979	814		

French

Patent No.	Ref.	Patent No.	Ref.	Patent No.	Ref.
972,455	887	1,157,006	172	1,160,849	211
972,456	888	1,160,106	198	1,164,023	225
1,101,682	890	1,160,107	199	1,171,805	253
1,147,722	143	1,160,108	200	1,171,806	254

(continued)

French (*continued*)

Patent No.	Ref.	Patent No.	Ref.	Patent No.	Ref.
1,181,893	283	1,293,597	563	1,360,643	759
1,210,101	400	1,294,752	645	1,363,890	796
1,210,632	223	1,299,556	674	1,367,487	740
1,210,637	250	1,300,770	671	1,367,558	754
1,211,629	403	1,307,117	706	1,369,447	844
1,214,892	280	1,307,490	628	1,369,703	783
1,217,675	295	1,309,809	495	1,372,908	790
1,226,657	449	1,320,229	643	1,378,024	813
1,228,366	363	1,326,931	683	1,378,500	803
1,228,507	374	1,331,159	692	1,385,548	863
1,229,071	370	1,333,311	696	1,385,684	805
1,231,875	459	1,333,966	689	1,393,595	825
1,234,905	493	1,334,305	301	1,393,730	832
1,235,424	474	1,334,518	762	1,394,915	869
1,241,563	431	1,335,508	677	1,395,558	768
1,241,564	438	1,337,602	700	1,395,993	835
1,247,235	442	1,339,286	705	1,399,201	883
1,255,077	535	1,342,435	744	1,399,515	884
1,258,434	546	1,347,881	798	1,403,867	839
1,261,808	576	1,347,976	717	1,405,589	846
1,276,804	607	1,348,550	799	1,405,656	853
1,278,574	537	1,351,387	763	1,411,704	872
1,284,280	554	1,354,773	720	1,414,477	862
1,283,856	613	1,358,415	811	1,415,030	856
1,288,829	646	1,358,757	812		

French Addition Patents

Addition patents	Ref.	Addition patents	Ref.
72,111 to 1,149,298	167	73,864 to 1,222,417	389
72,356 to 1,149,305	190	74,130 to 1,130,100	399
72,867 to 1,130,099	348	77,839 to 1,180,764	517
72,899 to 1,130,099	350	79,558 to 1,258,434	614
73,026 to 1,149,304	189	82,070 to 1,295,524	739
73,034 to 1,181,893	313	82,090 to 1,276,804	764
73,448 to 1,172,070	251	84,634 to 1,343,784	784

German

Patent No.	Ref.
15,445	21
1,004,803	65
1,015,226	894
1,024,240	895
1,040,249	898
1,043,635	149
1,047,437	38
1,049,585	90
1,056,829	175
1,065,618	163
1,079,328	49
1,080,304	426
1,081,230	386
1,083,051	412
1,084,026	238
1,084,408	458
1,084,917	427
1,085,335	144
1,086,047 (addn. to 1,070,825)	239
1,092,655	489
1,098,203	84
1,099,170	231
1,103,568	240
1,103,583	105
1,104,180	116
1,105,179	521
1,110,419	524
1,111,390	451
1,111,391	527
1,111,394	526
1,111,828	192
1,111,831	479
1,118,548	534
1,119,516	43
1,120,126	252
1,123,476	48
1,131,883	603
1,132,724	667
1,133,891 (addn. to 1,065,619)	219
1,134,201	591
1,134,834	476
1,137,555	577
1,138,227	584
1,138,934	530
1,151,660	676
1,156,238	617
1,156,985	618
1,161,423	748
1,171,157	794
1,174,991	733
1,182,830	801

Japanese

Patent No.	Ref.
646(59)	236
8,340(61)	440
9,992(61)	441
17,634(61)	519
17,993(61)	531
690(62)	556
3,300(62)	433
8,733(62)	557
8,735(62)	558
8,830(62)	624
9,837(62)	555
11,237(62)	622
11,437(62)	565
13,787(62)	520
13,881(62)	552
13,887(62)	623
18,387(62)	641
18,900(62)	568
1,238(63)	635
1,249(63)	615
2,138(63)	592
4,494(63)	662
7,134(63)	612
7,876(63)	598
7,878(63)	639
7,900(63)	638
9,431(63)	642
18,562(63)	620
22,490(63)	691
26,300(63)	599
90(64)	694
2,315(64)	579
18,956(64)	699
18,970(64)	719
18,980(64)	712
20,514(64)	779
3,718(65)	707
3,719(65)	722
7,072(65)	728
9,861(65)	821
9,964(65)	755
9,970(65)	723
10,427(65)	600
11,390(65)	711
12,185(65)	769
15,658(65)	718
15,821(65)	792
15,822(65)	793
16,155(65)	780
21,272(65)	771

Italian

Patent No.	Ref.
526,394	79
549,282	130
550,979	83
554,639	104
558,040	181
562,517	112
563,148	122
564,711	891
565,618	892
568,611	126
569,345	138
569,828	142
573,207	193
573,532	160
577,772	183
578,224	180
578,721	221
578,962	203
579,214	204
579,610	186
579,759	207
580,203	897
580,942	214
581,077	215
586,488	246
586,489	263
587,599	243
591,490	259
592,251	269
600,849 (addn. to 551,767)	188
602,489	327
604,774	131
608,998	308
640,015	573
652,608	682

Australian

Patent No.	Ref.
26,032/54	41
9,133/55	64
17,774/56	97
18,333/56	135
42,739/58	300
44,407/58	324
44,495/58	326
44,692/58	329
45,328/59	333
48,177/59	368
49,301/59	260
52,516/59	408
52,520/59	410
53,999/59	416
54,115/59	421
57,465/60	448
57,527/60	444
59,118/60	487
59,120/60	472
59,580/60	460
59,581/60	461
59,582/60	462
59,898/60	481
63,545/60	593
2,071/61	567
23,536/62	702
27,939/63	730
35,260/63	782

USSR

Patent No.	Ref.
111,857	896
116,268	899
118,976	900
127,392	484
131,084	902
146,083 (addn. to 131,084)	673
148,234	630
148,908 (addn. to 136,557)	690
157,108	715
158,063	742
159,657	800
165,537	855
166,094	816
166,443	861
170,675	770
173,404	842
173,946	829
173,949	819

Czechoslovakian

Patent No.	Ref.
106,405	651
106,425	652
108,656	653
108,675	684

Polish

Patent No.	Ref.
49,401	868

Netherlands

Patent No.	Ref.
65,127	886
75,532	889
288,606	817
299,793	857
64,01515	823
64,05132	837
64,05932	838
64,06144	841
64,06384	843
64,07752	847
64,08739	849
64,11609	858
64,12812	859
64,15317	865
65,00146	866
65,02357	870
65,07279	878

Canadian

Patent No.	Ref.
549,110	893
649,105	205

Irish

Patent No.	Ref.
152/64	822
680/64	877

Israeli

Patent No.	Ref.
15,962	695
17,225	743

Hungarian

Patent No.	Ref.
151,336	732

South African

Patent No.	Ref.
63/838	731

Austrian

Patent No.	Ref.
223,820	560

PATENT APPLICATIONS

Country	Number of patent applications
Great Britain	269
United States of America	205
Belgium	115
France	100
Germany	51
Japan	50
Italy	35
Australia	28
USSR	18
Netherlands	17
Czechoslovakia	4
Israel	2
Ireland	2
Canada	2
Austria	1
Hungary	1
South Africa	1
Poland	1
Total	902

APPENDIX II

Short abstracts of patents dealing with graft copolymerization or graft copolymers in general are presented n order of application date. The patent number, country of origin, publication date (if available), patentee, he backbone polymer, the grafted monomer, and the source reference are also included. Each abstract is given reference number which appears in the last column.

The abbreviation CA refers to *Chemical Abstracts*; this is followed by the volume and page number.

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	2,388,685	13.5.42	13.11.45	Dow Chemical	Poly(styrene)	Butadiene	A thermoplastic polymer which is flexible at temperatures below −50° is prepared by heating an aqueous emulsion of styrene (I) in a closed reaction at 75–100° until more than 90% of the I is polymerized, dispersing in the emulsion 2.3–3.5 moles of I, and completing the polymerization at a temperature of 75–100°. Air is excluded as far as possible during the entire process	*CA*, 40, 1346	1

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U.S.	2,422,550	20.10.42	17.6.47	Du Pont	Natural rubber	Vinyl compounds, e.g., methyl methacrylate, styrene, acrylonitrile, vinyl acetate, asymmetrical dichloroethylene, or 2-nitro-2-methyl propyl methacrylate	An aqueous medium containing about 0.1–2% of a perdisulfate salt and about 1–5% of a dispersing agent, such as dodecyl acid sulfate, is placed in a pressure vessel which is provided with a means of agitation. A mixture of rubber latex and unsaturated polymerizable compound is then added, oxygen is removed, and the mixture heated at 20° to about 80° until the polymerisation has proceeded to the desired extent	*CA*, 41, 5335	2
Brit.	604,708	30.11.45		Du Pont	Poly(vinylidene chloride), cellulose acetate, poly(vinyl alcohol), nonaethylene glycol, cellulose propionate, poly(methyl acrylate), or poly(vinyl acetate)	Ethylene	Ethylene is polymerized in the presence of performed polymers using a peroxide free radical initiator	Ceresa, R. J., *Block and Graft Copolymers*, Butterworths, London, 1962, p. 112	3
Brit.	624,079	22.12.45		Advance Solvents and Chemical Corp.	Natural rubber	Copolymers of meth-, or ethylacrylic acid and vinyl nitriles	Copolymers of methacrylic acid and a vinyl nitrile are added to natural rubber latex prior to full conversion and the stable latices heated to 212°C for 2 hr to complete the polymerization and effect grafting by transfer	Ceresa, p. 112	4

U. S.	2,524,045	5.6.46	3.10.50	Wingfoot Corp.	Polymeric carboxylic acid, e.g., poly(acrylic acid)	An amino acid, e.g., ε-caprolactam	An amino acid (I) having a single NH_2 and a single COOH separated by more than 4 atoms (and thus not subject to cyclization), or the corresponding esters, amides, and lactams is condensed with a polymeric carboxylic acid (II) of 10–500 COOH radicals per mole, or the corresponding ester, amides, and acid chlorides, I being present in the proportion of 500–20,000 moles for each mol. of II	*CA*, 45, 901	5
U. S.	2,542,771	16.4.47	20.2.51	Du Pont	Poly(vinylidene chloride), cellulose acetate, poly(vinyl alcohol), nonaethylene glycol, cellulose propionate, poly(methyl acrylate), poly(vinyl acetate), poly(hexamethylene diamine sebacate-hexamethylene diamine adipate-ε caprolactam)	Ethylene	Polymers are heated with benzoyl peroxide and ethylene under pressure to give grafting by transfer. The products are of improved water-resistance	*CA*, 45, 4486	6
U. S.	2,527,495	31.12.47	24.10.50	Shawinigan Resins Corp.	Poly(vinyl crotonaldehyde)	Vinyl monomers, e.g., vinyl acetate, acrylonitrile	Poly(vinyl crotonaldehyde) is heated with a vinyl monomer and a peroxide initiator for 30 min at 60°C to give grafting by transfer	*CA*, 45, 389	7

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	2,607,761	10.4.48	19.8.52	Industrial Research Institute, Univ. of Chattanooga	Polymers containing carboxylic acid groups, such as maleic anhydride copolymers of styrene, α-methyl styrene, vinyl acetate, or vinyl ethylhexyl ether, or acrylic acid copolymers of styrene or methyl methacrylate	Ethylene oxide, propylene oxide, 3,4-epoxy-1-butene, phenylethylene oxide, or epichlorohydrin	Copolymers of acrylic or methacrylic acid or of maleic anhydride are condensed with ethylene oxide at room temperature over several days in the presence of NaOH as catalyst	*CA*, 46, 11776	8
Brit.	652,401	8.6.48	25.4.51	Dunlop Rubber	Natural Rubber	Mixture of styrene and butadiene or isoprene	Graft copolymers are formed from persulfate initiation of styrene and a diene in the presence of natural rubber latex, by heating for 8 hr at 50°C	Ceresa, p. 113	9
U. S.	2,602,079	12.11.48	1.7.52	Petrolite Corp.	Polymers of dodecyl methacrylate; decyl, hexadecyl, octadecyl, and 9-octadecenyl methacrylates; dodecyl, hexadecyl, octadecyl, and 9-octadecenyl acrylates; vinyl laurate, vinyl stearate, and vinyl palmitate	Ethylene oxide	Ethylene oxide is condensed onto polyvinyl esters in xylene solution using sodium methoxide as a catalyst at 160°C. Multiple additions of ethylene oxide are made to give graft copolymers which emulsify with water	*CA*, 47, 5144	10

Brit.	667,291	5.3.49	27.2.52	Dunlop Rubber	Natural rubber	Mixture of styrene and a diene	Method as in Brit. 652,401 (see above) but using a hydroperoxide as the initiator	Ceresa, p. 113	11
Brit.	675,489	9.4.49	9.7.52	Dunlop Rubber	Natural rubber	Mixture of a nitrile and a conjugated diene	A polymerizable nitrile and a conjugated diene are copolymerized in the presence of natural rubber latex to give a graft copolymer by transfer using a free radical initiator	Ceresa, p. 113	12
U. S.	2,618,621	27.9.49	18.11.52	Union Carbide	Poly(vinyl chloride)	Polymerizable dimethacrylate of a poly(ethylene glycol)	Claims highly fluid plastisols which set on heating to semirigid solids consisting of 60–40% by wt vinyl chloride resin in 40–60% by wt dispersant comprising a nonpolymerizable plasticizer such as bis(2-ethyl hexyl) phthalate, and a polymerizable dimethacrylate of a poly(ethylene glycol). Suitable catalysts, inhibitors, and stabilizers are present	*CA*, 47, 3034	13
U. S.	2,556,158	29.9.49	12.6.51	Universal Oil Products	Natural rubber	Ethylene	Claims new and useful waxes produced by the organic peroxide-catalyzed condensation of ethylene with raw rubber in the presence of a saturated hydrocarbon diluent. The products are useful for the preparation of special greases and rubber extenders	*CA*, 45, 10674	14

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	2,649,434	27.5.50	18.8.53	Eastman Kodak	Poly(vinyl acetate), poly(*N*-methyl acrylamide), poly(*N*-methyl methacrylamide), poly(methyl α-carbethoxyamino acrylate), poly(citraconamide), poly(methyl methacrylate), poly (methacrylamide), poly(methyl α-acetoaminoacrylate), poly(*N*-isopropyl methacrylamide), or poly(methyl acrylate)	Acrylonitrile	Stable, homogeneous solutions of acrylonitrile (I) polymers are prepared by polymerizing I in the presence of a polymer such as poly (vinyl acetate), which has not been previously separated from its polymerization medium	*CA*, 47, 10862	15
U. S.	2,569,470	7.6.50	2.10.51	Eastman Kodak	Partially hydrolyzed poly(vinyl acetate)	Acrylonitrile	Acrylonitrile is polymerized in emulsion with a persulfate initiator in the presence of poly(vinyl acetate) to give grafting by transfer.	*CA*, 46, 272	16
U. S.	2,694,692	25.8.50	16.11.54	Dow	Natural or synthetic rubber	Styrene, or any other aromatic monovinyl compound	Natural and synthetic rubbers are heated with styrene and other monomers in the absence of added initiators to give graft copolymers by transfer. Agitation prevents gelation	*CA*, 49, 7284	17

U. S.	2,620,324	1.12.50	2.12.52	Eastman Kodak	Polymers of alkenyl carbonamides comprising the acryl, citracon-, itacon-, and maleamides alone or in conjunction with mono-ethylenically unsaturated compounds	Acrylonitrile	Polymers of acrylonitrile (I), the solutions of which are stable and do not separate into distinct layers on standing, and from which fibers of good dyeability can be spun, are obtained if I is polymerized in the presence of 10–40% of certain amide homo- or interpolymers in an aqueous or other solvent medium at 25–75° and in the presence of peroxides, azines, or keto azine as catalysts; emulsifiers; mercaptans as chain regulators, and reducing agents, e.g., $NaHSO_3$	*CA*, 47, 4100	18
U. S.	2,657,191	1.12.50	27.10.53	Eastman Kodak	Copolymer of two different mono-ethylenically unsaturated compounds containing a —CH═C< group (preferably a monomer containing a —CH═C═ group with either an acrylic ester, citraconamide, itaconamide, or vinyl ester, so that the copolymer contains 5–95% of each monomer)	Acrylonitrile	Acrylonitrile (I) is polymerized with preformed interpolymers (II) in the original reaction medium from II to yield polymers forming, in organic solvents, stable solutions from which homogeneous fibers with good dyeing properties and a softening point higher than II are spun	*CA*, 48, 3039	19

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	715,194	26.1.51		I.C.I.	High mol wt organic substance containing the C—H bond and having a mol wt >1000, e.g., starch, gelatin, poly(ethylene oxide), poly(acrylic acid), polymethacrylic acid, poly(methacrylamide), poly(vinylpyrrolidone), cellulose methyl ether, poly(vinyl alcohol), etc.	Acrylonitrile	Claims fiber forming polymers obtained by polymerising acrylonitrile in the presence of a water-soluble high mol wt organic substance such that the graft copolymer so formed contains between 5 and 40% by weight of the preformed polymer		20
Ger.	15,445	Brit. Appl. 26.1.51		I.C.I.	Equivalent to Brit. 715,194		See above		21
U. S.	2,703,284	8.2.51	1.3.55	Eastman Kodak	Lower fatty acid cellulose ester, such as cellulose tripropionate, cellulose acetate butyrate, or cellulose acetate	Alkyl acrylates such as ethyl acrylate, methyl acrylate, or methyl methacrylate	Subbing layer compounds that provide good adhesiveness, prevent "skidding," and have good flexibility are prepared by grafting a vinyl monomer onto a cellulose ester dispersed in water. Grafting is by transfer, initiated with a free radical catalyst	*CA*, 49, 6756	22
U. S.	2,646,418	25.5.51	21.7.53	Dow	Copolymer of butadiene and styrene	Styrene	Poly(butadiene-styrene) is grafted with styrene by heating with benzoyl peroxide at 90°C for 10 days to give grafting by transfer	*CA*, 47, 10898	23

U. S.	2,628,220	15.6.51	10.2.53	Standard Oil Development	Liquid poly(butadiene) latex	A mixture of SO_2 and an olefin	A liquid polybutadiene latex is agitated with a mixture of SO_2 and an olefin to give a graft copolymer with alternating side chains	Ceresa, p. 128	24
U. S.	2,741,650	8.11.51	10.4.56	Shawinigan Resins Corp.	Poly(vinyl acetate)	Styrene	Poly(vinyl acetate) is prepared using H_2O_2 as the initiator and styrene is then graft copolymerized onto the polymer using benzoyl peroxide. Grafting is by a transfer mechanism. The product is useful in adhesives and surface coatings	*CA*, 50, 12543	25
U. S.	2,649,435	5.12.51	18.8.53	Eastman Kodak	Formalated poly(vinyl alcohol)	Acrylonitrile	Formalated poly(vinyl alcohol) is grafted with acrylonitrile by transfer using a persulfate initiator	*CA*, 47, 10862	26
U. S.	2,719,138	17.1.52	27.9.55	Eastman Kodak	Polymer prepared from $CH_2{=}C\text{-}(R)\underset{\underset{O}{\Vert}}{C}N(R^1)\underset{\underset{O}{\Vert}}{C}(R^2)$ where R is H or an alkyl group containing 1–4 C atoms, R^1 is R or $C{=}O(R^2)$, and R^2 is an alkyl group containing 1–3 C atoms	Acrylonitrile	Claims fiber-forming copolymers prepared by polymerization of 60–95 parts acrylonitrile with 5–40 parts of said polymer or with an interpolymer containing 15–85% of above polymer and 15–85% of another ethylenic compound	*CA*, 50, 1332	27
Brit.	718,137	19.3.52		I.C.I.	Poly(vinyl alcohol)	Acrylonitrile or its mixture with a minor portion of one or more other monomeric vinyl compounds	Claims a composition comprising a grafted acrylonitrile polymer, ethylene carbonate, and water, wherein the weight of the ethylene carbonate is greater than that of the water		28

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	2,763,631	23.5.52	18.9.56	Eastman Kodak	Homopolymer emulsions of vinyl or vinylidene chloride	Acrylonitrile	Vinyl and vinylidene chloride are polymerized by persulfates as latices and acrylonitrile grafted on by polymerizing with additional initiator—a transfer process	*CA*, 51, 2304	29
U. S.	2,732,363	21.10.52	24.1.56	Eastman Kodak	Interpolymers prepared from compounds containing a $-\mathrm{CH}=\mathrm{C}<$ group, e.g., fumaramide	Acrylonitrile	Stable solutions of acrylonitrile (I) polymers are prepared by polymerization in the presence of preformed interpolymers which have not been separated from their polymerization media prior to the addition of I. The fibers obtained from these solutions have higher softening points than the interpolymers and are not subject to segmentation	*CA*, 50, 6062	30
U. S.	2,735,830	21.10.52	21.2.56	Eastman Kodak	Polymers and interpolymers of *N*-vinyl amides including *N*-vinylacylamides	Acrylonitrile or its mixture with another unsaturated monomer	Stable solutions of acrylonitrile (I) polymers are prepared by polymerizing I, or I and another unsaturated monomer in the presence of certain "live" preformed polymers and interpolymers of *N*-vinyl amides, i.e., polymers which have not been separated from their polymerization reaction mixture prior to the addition of I. Polymerization of the original mixture is substantially complete before the second polymerization is initiated	*CA*, 50, 8222	31
U. S.	2,735,831	21.10.52	21.2.56	Eastman Kodak	Poly(*N*,*N'*-dimethyl fumaramide)	Acrylamide, vinyl acetate, *N*-	Stable solutions of acrylonitrile (I) polymers are prepared by poly-	*CA*, 50, 8221	32

					or poly(*N*,*N'*-diisopropylfumaramide) etc.	methylmethacrylamide, fumaramide, methyl *N*-methylmaleamate, or methyl acrylate	merizing I in the presence of certain performed polymers in a 3-step polymerization		
Brit.	750,923	U.S. Appl. 6.11.52		Du Pont	Thermoplastic synthetic polymer, especially poly(ethylene) or nylon	Ethylenically unsaturated monomer (excluding any ethylenically unsaturated aliphatic hydrocarbon)	Claims a process for forming a grafted coating of a thermoplastic synthetic polymer or a film, sheet, rod, tube, or other article comprising contacting the article with said monomer in the presence of a catalyst capable of polymerizing the monomer		33
U. S.	2,731,439	17.11.52	17.1.56	Phillips Petroleum	Hydrogenated rubbery polymers	Acrylonitrile	Hydrogenated polybutadienes are heated with a peroxide initiator and acrylonitrile monomer to give grafting by transfer	*CA*, **50**, 11050	34
Brit.	733,093 (cf. Brit. 715,194 applied 26.1.51)	28.11.52		I.C.I.	Water-soluble, high mol wt organic substance, containing the C—H bond and having a mol wt >1000, e.g., poly(vinyl alcohol) or a water-soluble cellulose methyl ether	Acrylonitrile or its mixture with minor amounts, not greater than 15% of wt. of another copolymerizable material	Acrylonitrile is polymerized in aqueous medium together with a water-soluble polymer, so that the amount of high mol wt substance in the solid grafted acrylonitrile polymer or copolymer so formed is between 5 and 40% by wt. The polymer or copolymer is then separated from the aqueous phase, e.g., by filtration, and the aqueous phase so separated, with, if desired, any aqueous washings of the polymer or copolymer is used again in the polymerization process		35

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	2,755,270	21.11.52	17.7.56	Firestone Tire and Rubber	Rubbery butadiene polymers	Styrene	Claims blends of styrene-type resins, graft copolymers of styrene with a rubber butadiene polymer or copolymers, and rubbery butadiene polymers or copolymers which provide compositions with high impact strength, high heat distortion point, good low temperature properties, and high modulus of elasticity which are suitable for injection molding and extrusion, and which, in sheet form, can be hot formed into various shapes	*CA*, 50, 16179	36
U. S.	2,837,496	31.12.52	3.6.58	Hercules Powder	Polymer hydroperoxide of a vinylidene compound or styrene	Monomer polymerizable by a free radical mechanism, e.g., methyl acrylate, vinyl acetate, acrylamide, or styrene	Claims a process for preparing a graft copolymer by decomposing a polymer hydroperoxide of a vinylidene compound under conditions such as to yield free radicals in the polymer chain, in the presence of one or more monomers capable of being polymerized by a free radical mechanism	*CA*, 53, 1851	37
Ger. (D.A.S.)	1,047,437	U.S. Appl. 15.1.53		Union Carbide	Polybutadiene	Styrene	Butadiene-styrene graft copolymers are obtained by free radical polymerization of butadiene under alkaline conditions at below 60°C to polybutadiene of specific viscosity at least 0.3, followed by graft copolymerisation with styrene		38
U. S.	2,839,491	23.3.53		Eastman Kodak	Terpolymer of a mixture of monomers consisting	Acrylonitrile	Claims a graft copolymer of from 75 to 90% by wt of acrylonitrile and from 25 to 10% by wt of a pre-		39

				of methyl acrylate, vinyl alcohol, and a *N*-alkyl acrylamide		formed terpolymer. Said terpolymer is obtained by heating a binary copolymer consisting of methyl acrylate and vinyl acetate with a primary monoalkylamine containing from 1–4 C atoms, in a reaction medium consisting of a saturated monohydric aliphatic alcohol containing from 1–3 C atoms, until from 50 to 90% by weight of the said methyl acrylate units have been converted to the corresponding *N*-alkyl acrylamide units and substantially 100% by weight of the said vinyl acetate units have been converted to vinyl alcohol units	
U. S.	3,062,777	14.4.53	Union Carbide	Rubber butadiene-styrene copolymer containing between 3 and 50% by wt of bound styrene	Styrene	Claims the polymerization product of a reaction charge of styrene monomer and a rubbery butadiene-styrene copolymer, the reaction being continued to a stage where the initial weight of the butadiene-styrene copolymer constitutes from 20 to 60% of the reaction product solids and in which from 3 to 100 parts of styrene have been reached on 100 parts of the copolymer	40
Austral.	26,032/54	U.S. Appl. 14.4.53 24.3.54	Union Carbide	Equivalent to U. S. 3,062,777		See above	41
Brit.	749,494	U.S. Appl. 14.4.53	Union Carbide	Equivalent to U. S. 3,062,777		See above	42

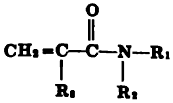
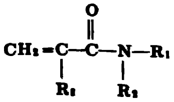
(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Ger.	1,119,516	U.S. Appl. 14.4.53		Union Carbide	Equivalent to U. S. 3,062,777		See above		43
Brit.	788,651	15.4.53		British Rubber Producers Research Assoc.	Natural rubber latex	Methyl methacrylate styrene, ethyl acrylate, divinyl benzene, or mixtures of the above	Monomers are polymerized in natural rubber latex using a hydroperoxide and a polyamine as a low temperature redox initiation system		44
Brit.	742,900	15.7.53		I.C.I.	Poly(vinyl alcohol)	Acrylonitrile	Claims an improved process for making shaped articles such as filaments, yarns, films, and the like, in which acrylonitrile is polymerized in an aqueous medium alone, or in the presence of small amounts of other copolymerizable material together with more than 60% by wt of a water soluble poly(vinyl alcohol) and the viscous aqueous solution obtained is then extruded through a disc or a spinneret into a coagulating bath, preferably containing a saline solution		45
U. S.	2,780,605	16.7.53	5.2.57	United States Rubber	Natural rubber latex	Styrene	Styrene is polymerized by a persulfate initiator in the presence of natural rubber latex so that less than 5% of the total polymerized styrene is present in the latex as free poly(styrene) particles	*CA*, 51, 7049	46
U. S.	2,802,808	31.7.53		Firestone Tire and Rubber	Butadiene rubber substrate	A mixture of monomers containing 50–90%	Claims a strong, impact resistant, polycomponent polymeric composition comprising (A) a styrene-		47

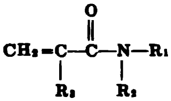
					of a compound selected from the group consisting of styrene and α-methyl styrene and 10–50% of a compound selected from the group consisting of acrylonitrile and methacrylonitrile	acrylonitrile type resin, (B) a graft copolymer of a styrene-acrylonitrile type mixture of monomers upon a butadiene rubber, and (C) a butadiene rubber	
Ger.	1,123,476	U.S. Appl. 8.9.53	O. W. Burke, Jr.	Natural or synthetic high polymer	A monomer or monomer mixture, of which at least one monomer must contain groups suitable for crosslinking if the core polymer is uncrosslinked	Insoluble crosslinked graft copolymers of colloidal particle size are prepared by polymerizing monomers optionally containing crosslinking bonds, in the presence of preformed polymers. The monomer is polymerized in the presence of the preformed polymer distributed in a colloidal emulsion and in the presence of a catalyst, the polymerization being carried out until the particles obtained are insoluble. Normal polymer emulsifiers or water-soluble polymers may be used as emulsifiers in the graft polymerization	48
Ger. (D.A.S.)	1,079,328	22.10.53	Beck and Co.	Rubbery polymers	Unsaturated hydrocarbon nitriles or esters	Rubbery polymers of medium molecular weight made by polymerization with sodium are modified by graft copolymerization of unsaturated hydrocarbon nitriles or esters	49

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	757,523	30.10.53		Distillers	Natural rubber	Polystyrene	Natural rubber, polystyrene, and an organic peroxide or hydroperoxide are blended together on a hot mill to give a crosslinked graft copolymer which is compatible with the mixture on further milling		50
U. S.	2,859,201	9.11.53	4.11.58	Phillips Petroleum	Copolymers of conjugated dienes and acid type monomers, e.g., butadiene-acrylic acid	Polymerizable substrate	Graft type polymers are produced by copolymerising conjugated dienes with acid type monomers and dissolving the resulting acidic copolymers in aqueous bases. A suitable polymerizable material is then caused to polymerise in the aqueous solution causing grafting at the points of unsaturation	*CA*, 53, 23109	51
U. S.	2,802,809	30.11.53		Firestone Tire and Rubber	A diene rubber	A styrene-acrylonitrile type mixture	Claims a composition comprising (A) a vinyl chloride resin blended with (B) a graft copolymer of a styrene-acrylonitrile-type mixture upon a diene rubber		52
U. S.	3,019,208	18.1.54		Firestone	Homopolymer of an alkyl ester of acrylic acid, the alkyl group of which contains 1–10 C atoms	Vinyl chloride or a mixture of vinyl chloride and up 15% of a copolymerizable monoethylenically unsaturated monomer	Vinyl chloride or its mixture with another monoethylenically unsaturated monomer is emulsified in an aqueous emulsion of a poly(acrylate) and then heated to 30–70° C in the presence of potassium persulfate		53
U. S.	2,838,470	3.2.54		Eastman Kodak	Copolymer of from 50 to 99% by wt of an amide rep-	A monomer mixture consisting of from 85.0 to	Claims a resinous fiber-forming graft copolymer prepared by polymerizing an acrylonitrile		54

				resented by the following formula,  $CH_2{=}\underset{R_3}{\underset{\vert}{C}}—\overset{O}{\overset{\Vert}{C}}—\underset{R_2}{\underset{\vert}{N}}—R_1$ wherein R_1 and R_2 represents a H or an alkyl group of C 1–4 and R_3 represents a H or CH_3, and from 50 to 1% by wt of a compound selected from the group consisting of a dissimilar amide represented by the above general formula and acrylonitrile	99.5% by wt of acrylonitrile and from 15.0 to 0.5% by wt of a monomer represented by the above general formula	mixture in an aqueous dispersion of said copolymer	
U. S.	2,879,253 and 2,879,254	3.2.54	Eastman Kodak	Homopolymer of  $CH_2{=}\underset{R_3}{\underset{\vert}{C}}—\overset{O}{\overset{\Vert}{C}}—\underset{R_2}{\underset{\vert}{N}}—R_1$ wherein one of the R_1 and R_2 represents a C_{1-4} alkyl group and the other may be H or C_{1-4} alkyl, and R_3, H or CH_3	Mixture of from 85 to 99.5% acrylonitrile and 15 to 0.5% of vinyl chloride, vinylidene chloride, methacrylonitrile, styrene, or other specified monomers	Claims a resinous fiber forming graft copolymer prepared by heating a mixture of water, a peroxide polymerization catalyst, and 40–50 parts of said homopolymer with 60–95 parts by wt of an acrylonitrile mixture	55

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	2,583,360	3.2.54		Eastman Kodak	A polymer of the type  $CH_2=C(R_3)-C(=O)-N(R_2)-R_1$ where R_1 is C_{1-4}, R_2 is H or C_{1-4}, and R_3 is H or Me	Monomeric mixture consisting of 85 to 100 % acrylonitrile and 0 to 15 % of a monomer containing a single $CH_2=C<$ group	A graft copolymer is prepared by continuously introducing into a polymerization reactor vessel (1) water, (2) 60–95 parts of an acrylonitrile mixture, (3) a peroxide catalyst, and (4) 40–5 parts of a preformed polyamide		56
Brit.	767,642	U.S. Appl. 16.2.54		Monsanto	Polybutadienes	Styrene	Liquid polybutadienes are dissolved in styrene monomer and the styrene polymerized in three stages at 90, 120, and 180°C, respectively. Grafting occurs by transfer		57
Brit.	791,453	Fr. Appl. 3.3.54	5.3.58	Polyplastic	Natural rubbers	Polymerizable monomers	Graft-type polymers are prepared by conducting the polymerization of monomers in the presence of previously decomposed, unstable polymers. Decomposition of the catalyzing polymers is effected by oxidation which can be conducted in either solutions or emulsions of the polymer. The unstable polymers supply free radicals which are capable of initiating polymerization of other monomers. The process is particularly suitable for natural rubbers which form graft-type copolymers of superior oil and solvent resistance	*CA*, 52, 14210	58

Brit.	766,528	13.4.54	23.1.57	Midland Silicones	Polysiloxanes or silans	Trifluorochloroethylene	Polysiloxanes, silans, and related materials are heated with trifluorochloroethylene and other monomers together with a peroxidic compound. Graft copolymerization occurs by a transfer process	*CA*, 51, 10121	59
U. S.	2,849,419	15.4.54		Firestone Tire and Rubber	Polymeric vinylidene chloride resin	C_{1-10} alkyl acrylate	Claims on oriented filament composed of a copolymer of a vinylidene chloride resin with another monoethylenically unsaturated monomer with grafted polyacrylate side chains		60
U. S.	2,840,447	28.4.54	24.6.58	Du Pont	Poly(vinyl acetate)	Acrylonitrile or any other monomer which polymerizes to form a stable emulsion	Graft polymers of acrylonitrile and monomers are prepared by successive polymerizations in an aqueous dispersion with free radical initiators, and shaped objects, particularly fibers, are formed directly from the dispersions, without melting or dissolving the graft polymers prior to extrusion	*CA*, 52, 19244	61
Brit.	778,265	U.S. Appl. 30.4.54	3.7.57	Monsanto	A preformed, gel-containing rubbery butadiene-acrylonitrile interpolymer	Mixture of styrene and acrylonitrile	Styrene-acrylonitrile rubber is dispersed in a mixture of styrene and acrylonitrile and thermally polymerized in 3 stages; 24 hr at 90°C, 24 hr at 120°C, and 8 hr at 180°C. Grafting is by transfer	*CA*, 51, 17240	62

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	771,926	12.6.54	10.4.57	Distillers	A "hydroxyalkylated" poly (styrene)	Polymerizable cyclic ether; must be capable of polymerizing by the opening of the ether ring under the influence of the basic catalyst to form linear polymeric ethers which contain ether oxygen atoms linking ethylene, propylene, or substituted ethylene or propylene residues together	Claims a process for the production of a graft copolymer comprising heating a polymerizable cyclic ether in a substantially anhydrous medium containing a hydroxyalkylated poly(styrene) and an alkali metal or an alkali metal oxide, hydroxide, hydride, or alkoxide as catalyst for the reaction, whereby polymerisation of the cyclic ether with the formation of a graft copolymer occurs	*CA*, 51, 10960	63
Austral.	9,133/55	Brit. Appl. 12.6.54	16.5.55	Distillers	Equivalent to Brit. 771,926		See above		64
Ger. (D.A.S.)	1,004,803	Brit. Appl. 12.6.54	10.6.55	Distillers	Equivalent to Brit. 771,926		See above		65
Brit.	766,585	18.6.54		Monsanto	Natural or synthetic rubber	Styrene	Up to 25% of natural or synthetic rubber is dissolved in styrene monomer and polymerisation is effected thermally in 3 stages,		66

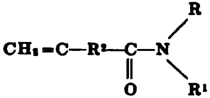
							each successive stage at a higher temperature until complete polymerization is effected. Grafting takes place by a transfer process		
U. S.	2,882,290	30.7.54		Eastman Kodak	A preformed homopolymer of a specified vinyl pyridine	A mixture of monomers consisting of 85–99.5% acrylonitrile and 15–0.5% of at least one different monomer selected from a specified range	Claims a graft copolymer of said constituents, the acrylonitrile amounting to at least 60% and the vinylpyridine at least 5% of the graft copolymer		67
U. S.	2,841,569	30.8.54	1.7.58	Union Carbide	Poly(ethylene)	Acrylonitrile or methacrylonitrile	Graft copolymers of poly(ethylene) (I) and acrylonitrile (II) are prepared by slow addition of II to a solution of I and a free radical catalyst in benzene, heptane, hexane, or carbon tetrachloride. The products can be molded readily and suffer little color change if 1% of an acidic substance such as tetrachlorophthalic anhydride is added	*CA*, 52, 16800	68
Brit.	814,393	U.S. Appl. 30.8.54	3.8.56	Union Carbide	Poly(ethylene)	Vinyl chloride or vinyl butyrate, vinyl-2-ethyl hexoate, vinylene carbonate, and vinyl propionate	Poly(ethylene) is dissolved in benzene at 70° under N, Bz_2O_2 added followed by vinyl chloride and the mixture heated in a sealed reactor for 90 hr at 70° and 95 psi. The polymers are nearly transparent and can be creased and bent without blushing	*CA*, 53, 18554	69

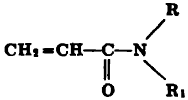
(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	2,947,718	30.8.54	2.8.60	Union Carbide	Poly(ethylene)	Vinyl ester of a carboxylic acid	A preformed, normally solid poly(ethylene) in an aromatic solvent, and a vinyl ester of a carboxylic acid are treated with benzoyl, hydroxyheptyl, methyl ethyl ketone, cyclohexanone, *p*-chlorobenzyl, or ditertiary-butyl diperphthalate, to form a homogeneous mixture of ethylene homopolymer, a homopolymer of the vinyl ester, and a graft copolymer of poly(ethylene) and the vinyl ester	*CA*, 54, 26013	70
U. S.	2,947,719	9.9.54		Union Carbide	Poly(ethylene)	Vinyl chloride	Claims a vinyl chloride-polyethylene graft copolymer prepared by reacting vinyl chloride, in the presence of benzoyl peroxide, with a preformed, normally solid poly(ethylene), said P|E bieng dissolved in an aromatic solvent		71
U. S.	2,842,518	13.9.54	8.7.58	Borg-Warner Corp.	Poly(chloroprene)	Mixture of vinylidene chloride, and acrylonitrile	Mixtures of vinylidene chloride and acrylonitrile, and in some cases styrene, are free radically polymerized in the presence of poly(chloroprene) latex to give complex graft copolymers by transfer	*CA*, 52, 21251	72
U. S.	2,842,519 (cf. Brit. 771,926 (*CA*, 51, 10960) applied 12.6.54)	13.9.54	8.7.58	Distillers	Copolymer of styrene and an unsaturated carboxy lic acid	Polymerizable cyclic ether selected from the group consisting of ethylene oxide and its alkyl or alkenyl homologs containing	Claims a process for the production of a graft copolymer which comprises polymerizing a cyclic ether and trimethylene oxide in the presence of a styrene-unsaturated carboxylic acid copolymer by heating the mixture in an anhydrous medium to a temperature above 80°C. The polymerization	*CA*, 52, 15965	73

						not more than 4 carbon atoms	catalyst is selected from the group consisting of the alkali metals and the alkali metal oxides, hydroxides, hydrides, and alkoxides		
U. S.	2,908,657	15.9.54	13.10.59	United States Rubber	Polyurethanes	Starch	Polyesters having terminal isocyanate groups are coupled to starch to give graft copolymers	*CA*, 54, 12666	74
Brit.	779,557	1.10.54	24.7.57	I.C.I.	Partially hydrolyzed poly(vinyl acetate)	Vinyl acetate	Vinyl acetate is polymerized rapidly with a persulfate catalyst by emulsifying it in the presence of partially hydrolyzed poly(vinyl acetate) and an alkali. Grafting is by a transfer mechanism	*CA*, 51, 18701	75
Brit.	820,930 Addition to Brit. 779,043 divided out of Brit. 820,207	U.S. Appl. 15.10.54	30.9.59	O. W. Burke Jr.	Polystyrenes	Vinyl monomers, e.g., styrene, methyl methacrylate, butadiene, etc.	Vinyl monomers are polymerized in the presence of aqueous dispersions of colloidal crosslinked styrene copolymers (vinylic fillers) using a free radical catalyst to give complex graft copolymers by transfer	*CA*, 55, 4043	76
U. S.	2,865,872	22.10.54		Eastman Kodak	Cellulose	Mixture of acrylonitrile with at least one other monomer	Graft copolymerizing 5–50% of a cellulose compound having 10–70% of the hydroxyl groups in free form with 95–50% of a monomeric material consisting of 75–98% acrylonitrile and 25–2% of at least one other monomer in the presence of a polymerization catalyst and an alkyl mercaptan. The product forms a high softening dyeable fiber		77
Brit.	816,579	Ital. Appl. 18.11.54	15.7.59	Montecatini	Poly(acrylamide), poly(vinyl alcohol), poly(acrylic acid)	Styrene	Claims a method of grafting styrene to preformed polymers by transfer using a persulfate catalyst	*CA*, 53, 20913	78

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Ital.	526,394	18.11.54	16.5.55	Montecatini			The polymerization of vinyl monomers in water suspension is improved if "graft" copolymers (prepared as above) are used as the dispersing agents instead of starch, gelatin, cellulose derivatives, etc. The formation of agglomerates and scale in the reactor is avoided	*CA*, 52, 15134	79
U. S.	2,899,405	26.11.54	11.8.59	Eastman Kodak	Preformed polymer or interpolymer of a vinylic amide or amate or an acrylate	Mixture of vinyl chloride, vinylidene chloride, and another monomer	Vinyl chloride and vinylidene chloride are polymerized in the presence of polyamide polymers and copolymers to give grafted copolymers by a transfer mechanism	*CA*, 53, 22974	80
U. S.	2,921,044	26.11.54	12.1.60	Eastman Kodak	Copolymer consisting of 1–99% by wt  $CH_2{=}C{-}R^2{-}\overset{}{\underset{\overset{\parallel}{O}}{C}}{-}N{<}^{R}_{R^1}$ in which R and R^1 are H or alkyl groups of 1–4 C atoms, and R^2 is H or Me, and 99–1% by wt of a material different from the above amide but having the same structure, or acrylonitrile or methyl methacrylate	Mixture of vinyl chloride or vinylidene chloride with another vinylic monomer	A process is described to graft-copolymerize, at 15–75° in H_2O and in the presence of a peroxy-polymerization catalyst 60–95% by wt, a material comprising 30–99% vinyl chloride or vinylidene chloride and 70–1% acrylonitrile, methacrylamide, or methacrylonitrile, with 40–5% of an unisolated preformed copolymer. Fibers obtained from these polymers have an excellent affinity for dyes	*CA*, 54, 9368	81

U. S.	3,026,289	26.11.54		Eastman Kodak	Homopolymer of a material of formula  $CH_2{=}CH{-}C({=}O){-}N(R)(R_1)$ where R and R_1 are H or alkyl of 1–4 C atoms	Monomeric mixture comprising 30–99% of vinyl chloride or vinylidene chloride and 70–1% of acrylonitrile, vinyl acetate, methyl acrylate, or methacrylonitrile	A process is described to graft copolymerize at 15–75° in H_2O and in the presence of a peroxy polymerization catalyst a mixture of 5–40% of said unisolated homopolymer and 95–60% of a specified monomeric material		82
Ital.	550,979	U.S. Appl. 26.11.54		Eastman Kodak	Equivalent to U. S. 2,899,405		See above		83
Ger.	1,098,203	U. S. Appl. 26.11.54		Eastman Kodak	Equivalent to U. S. 2,899,405		See above		84
U. S.	2,867,601	29.11.54	6.1.59	Minesota Mining and Manufacturing	A polymer prepared from permaleic acid and $CF_2{=}CFCl$ or other fluorosubstituted monoolefins containing at least 2 F atoms	Styrene, butyl acrylate, or other ethylenically unsaturated monomer	Claims a graft copolymer comprising (A) a copolymer of a halogen substituted monoolefin containing at least 2 fluorine atoms and containing no halogen other than fluorine chlorine, and bromine, and permaleic acid and (B) an ethylenically unsaturated monomer	*CA*, 53, 6691	85
U. S.	2,901,458	30.12.54	25.8.59	Esso Research and Engineering	Rubbery copolymer consisting of monomeric isobutylene and a conjugated diolefin of 4–6 C atoms	Polar organic monomer containing a terminal $CH_2{=}C{<}$ group	Claims a process comprising reacting as the sole ingredients 100 parts by weight of a rubbery copolymer with about 5–200 parts by wt of a polar organic monomer and at least one element selected from the group consisting of oxygen and nitrogen, in the presence of about 1–10 volumes of inert diluent, and in the presence of a peroxide catalyst, at a temperature of about 50–250°C for about 1–10 hr	*CA*, 54, 949	86

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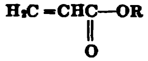
Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	819,651	Can. Appl. 8.2.55		Polymer Corp.	Butadiene-1,3-styrene copolymer or poly(styrene), poly(butadiene)	Butadiene-1,3-styrene, acrylamide, butyl methacrylate, methyl methacrylate, or acrylonitrile	Butadiene styrene latices are peroxidized by ozonized oxygen and then used as initiators for graft copolymerization using $FeSO_4$ and ethylenediamine tetraacetic acid as redox activators		87
Brit.	828,895	14.2.55 15.3.56	24.2.60	British Rubber Producers Research Assoc.	Natural or synthetic rubber	Vinyl monomer, e.g., methyl methacrylate	A natural or synthetic rubber is masticated while cold under oxygen-free conditions in the presence of a polymerizable vinyl monomer	*CA*, 54, 11536	88
Brit.	788,175	18.2.55	23.12.57	Distillers	Polynuclear aromatic hydrocarbon polymer, e.g., styrene-α-vinylnaphthalene copolymer	Vinyl monomer, e.g., acrylonitrile, styrene, vinyl acetate, or methyl methacrylate	Graft copolymers are prepared by UV radiation of a polynuclear aromatic hydrocarbon polymer dissolved in a polymerizable vinyl compound	*CA*, 52, 9668	89
Ger.	1,049,585	Brit. Appl. 18.2.55		Distillers	Equivalent to Brit. 788,175		See above		90
Brit.	778,102	25.2.55		Styrene Products	Natural or synthetic rubber latex	Vinylpyridine and at least one other polymerizable compound containing an ethylenic double bond	A mixture of two monomers is added to natural or synthetic rubber latex, together with stabilizers and a hydroperoxide catalyst, in three or less separate stages, the latex being heated after each monomer addition. Graft copolymerization occurs by transfer		91
U. S.	2,843,561	29.3.55	15.7.58	Dow	Butadiene-styrene copolymer	A mixture of monomers consisting of 50–60% of at least	A styrene-butadiene copolymer is heated with said monomer mixture (e.g., styrene-ethyl acrylate) in the presence of benzoyl per-	*CA*, 52, 19257	92

						one monovinyl aromatic hydrocarbon and 40–50% of at least one acrylate of the formula  $H_2C{=}CHC(=O){-}OR$ in which R is an alkyl radical containing 1–4 carbon atoms	oxide to give grafting by transfer		
Brit.	820,120	7.4.55 25.4.55	16.9.59	Du Pont	Synthetic addition product, i.e., formed from polymerising styrene, acrylic acid esters, vinyl halides, vinylidene halides, vinyl compounds containing S, N, or P. or acrylonitrile	Organic modifier, e.g., dodecafluoroheptyl alcohol or other fluorocarbon derivatives, a polymethylenediamine, bis(3-aminopropoxy) ethane, or an addition polymerisable compound containing one or more ethylenic double bonds	A synthetic addition product is modified by subjecting it to ionising radiation while in intimate contact with a modifier. The latter consists of at least one organic compound which, when chemically bonded to the addition polymer as a result of the irradiation, causes an appreciable change in one or more of the properties of the product. The modifier is dispersed in or diffused into the addition product; or, when it is desired to modify only the surface of a shaped article, it is applied to the surface as a solution	*CA*, 54, 5161	93
Brit.	838,413	U. S. Appl. 16.4.55 25.4.55 16.8.56	22.6.60	Du Pont	Synthetic condensation polymer, e.g., nylon	Monomers containing free COOH groups or carboxylate salt groups and nonaromatic carbon-carbon unsaturation, e.g., maleic anhydride	The condensation polymer is soaked in an aqueous solution of said monomer and irradiated with electrons from a Van de Graaff generator to form a graft copolymer with improved properties	*CA*, 54, 25867	94

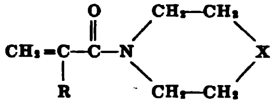
(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	809,838	Fr. Appl. 29.4.55	4.3.59	Centre Nationale de la Recherche Scientifique	Poly(vinyl chloride), poly(styrene), poly(ethylene), cellulose acetate, poly(methyl methacrylate), nylon, or polyterephthalate (Process Claim)	Acrylonitrile or acrylamide	Graft copolymers are prepared by subjecting a polymer to ionizing radiation in the presence of oxygen and then contacting the irradiated polymer with a polymerizable monomer in the absence of oxygen	*CA*, 53, 11894	95
Belg.	547,078	Fr. Appl. 29.4.55 31.5.55 17.4.56		Centre Nationale de la Recherche Scientifique	Equivalent to Brit. 809,838		See above		96
Austral.	17,774/56	Fr. Appl. 29.4.55 31.5.55 26.4.56		Centre Nationale de la Recherche Scientifique	Equivalent to Brit. 809,838		See above		97
Brit.	786,142 addition to Brit. 766,528	U.S. Appl. 2.5.55	30.3.57	Midland Silicones	Trimethyl end-blocked dimethylpolysiloxane	Trifluorochloroethylene	Trifluorochloroethylene is heated in an atmosphere of nitrogen in an autoclave at 131° for 17 hr in the presence of said polymer, ditertiary butyl peroxide, and a small amount of magnesium oxide	*CA*, 52,	98
Brit.	791,765	11.5.55	12.3.58	I.C.I.	Poly(acrylonitrile) (Process Claim)	Vinyl alcohol	A process for the prevention of discoloration in grafted acrylonitrile polymers comprises heating them with an aqueous acidic solution of an aldehyde. The polymer may be in the form of a filament or yarn	*CA*, 52, 19162	99

Brit.	766,686	17.5.55	23.1.57	Distillers	Natural rubber	Methyl methacrylate	Claims a tough poly(styrene) composition containing a graft copolymer of methyl methacrylate or natural rubber	*CA*, 51, 11761	100
U. S.	2,891,018	Brit. Appl. 17.5.55	16.6.59	Distillers	Equivalent to Brit. 766,686		See above	*CA*, 53, 15642	101
Brit.	801,528	Fr. Appl. 31.5.55	17.9.58	Centre Nationale de la Recherche Scientifique	Poly(ethylene), poly(vinyl chloride), polyamides, poly(styrene), rubber, cellulose, poly(methyl acrylate), polyesters, polyfluoroethylene, or poly(isobutylene) (Process Claim)	Vinyl chloride, styrene, vinylidene chloride, isoprene, butadiene, or acrylonitrile	Claims a process for the production of graft copolymers wherein a polymer is exposed to the action of ionizing radiation while in contact with at least one compound selected from the group consisting of vinyl and divinyl monomers, the polymer being constituted of a monomer different from that of the group. Irradiation is carried out in the absence of oxygen	*CA*, 53, 23080	102
Belg.	547,688	Fr. Appl. 31.5.55	9.5.56	Centre Nationale de la Recherche Scientifique	Equivalent to Brit. 801,528		See above		103
Ital.	554,639	Fr. Appl. 31.5.55 25.5.56		Centre Nationale de la Recherche Scientifique	Equivalent to Brit. 801,528		See above		104
Ger.	1,103,583	Fr. Appl. 31.5.55		Centre Nationale de la Recherche Scientifique	Equivalent to Brit. 801,528		See above		105

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	2,907,675	8.7.55	6.10.59	Du Pont	Poly(ethylene), poly(ethylene terephthalate), poly(hexamethylene-sebacamide), poly(vinyl chloride) (Process Claim)	Ethylenically unsaturated monomer	Polymeric films are irradiated by high energy particles while immersed in a nonoxidising medium capable of forming free radicals. The irradiated surface is then immersed in an ethylenically unsaturated monomer to form an adherent coating. Alternatively, the film may be immersed in the monomer while being irradiated	*CA*, 55 24102	106
U. S.	3,111,424	8.7.55		Du Pont	Poly(ethylene) (Process Claim)	Methyl methacrylate	A synthetic polymer substrate, particularly film, is subjected to ionizing irradiation in an inert atmosphere (e.g., N_2) and immediately contacted with an ethylenically unsaturated monomer to form a polymeric coating		107
Brit.	801,531	U. S. Appl. 8.7.55		Du Pont	Equivalent to U. S. 3,111,424		See above		108
U. S.	2,850,479	8.8.55		Chemstrand Corp.	Copolymer of vinyl pyridine and acrylic acid	Monomeric mixture of at least 85% acrylonitrile and up to 15% of another monoolefinic monomer	Said monomeric mixture is polymerized in the presence of a vinylpyridine acrylic acid copolymer with a watersoluble peroxy or azo catalyst to form a graft copolymer		109
Brit.	832,692	Can. Appl. 20.9.55		Polymer Corp.	Naturally occurring polymer (with the exception of natural rubber), e.g., protein or a polysaccharide	Ethylenically unsaturated monomer, e.g., butadiene, 1,3-styrene, acrylonitrile	A process for grafting an ethylenically unsaturated polymerizable compound onto a preformed naturally occurring polymer or a derivative thereof which comprises oxygenating the polymer in an		110

						aqueous dispersion or solution with either oxygen or ozone and subsequently polymerizing the oxygenated polymer with a polymerizable compound in a free radical aqueous dispersion or solution system	
U. S.	2,798,061	28.9.55	Eastman Kodak	Copolymer formed from 50–100% of a monomeric material of formula  wherein R is H or Me and X is O, S or a —CH$_2$— group and from 50–0% of a different monoethylenically unsaturated monomer containing a single CH$_2$C < group	A monomer mixture consisting of from 30–100% of a member selected from acrylonitrile and methacrylonitrile and 70–0% of a member selected from vinyl chloride and vinylidene chloride	Claims a resinous graft copolymer of said polymer and monomer mixture	111
Ital.	562,517	U. S. Appl. 5.10.55	Oliver Burke, Jr.			Claims graft vinyl fillers which comprise macromolecular products with collodial size particles, wherein one component is a base polymer the second is grafted on to it, said particles being crosslinked until insoluble. Also claims elastomers and other organic polymer materials containing said fillers	112

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	2,806,842	24.10.55		Colgate-Palmolive	Copolymer of styrene and a carboxylic acid amido alcohol	Alkylene oxide	Claims an alkylene α, β oxide addition product of a copolymer of (a) styrene and (b) an α, β ethylenically unsaturated carboxylic acid amido alcohol, said addition product being substantially free of ionic groups		113
Brit.	817,684	4.11.55 4.9.56	6.8.59	National Research Development Corp.	Polymers containing F, Cl, or Br attached to an aliphatic carbon atom	Aromatic hydrocarbon or an olefinic compound	Said polymers are treated in the presence of a Friedel-Crafts catalyst with an aromatic hydrocarbon which is capable of being alkylated by means of, or an olefinic compound which is capable of being polymerized by, a Friedel-Crafts catalyst	*CA*, 54, 11577	114
Brit.	832,193	9.11.55 7.5.56	4.6.60	British Rubber Producers Research Association	Natural or synthetic resins, e.g., poly(styrene), poly(hexamethylene adipate) poly(ethylene) or shellac	Methyl methacrylate, styrene, or vinyl acetate	Graft or block copolymers are made by the mastication, in the absence of oxygen, of said monomers with natural or synthetic resins	*CA*, 54, 14799	115
Ger.	1,104,180	Brit. Appl. 9.11.55 7.5.56		Natural Rubber Producers Research Association	Nonrubbery polymer	Olefin monomer	Production of graft copolymers from a mixture of a nonrubbery polymer, an olefin monomer and if necessary a plasticizer for the polymer, using proportions such that the mixture is rubberlike at mastication temperature		116
U. S.	2,972,593	10.11.55		United States Rubber	Poly(butadiene) or copolymers of butadiene with styrene	Styrene-acrylonitrile mixture	Claims a vulcanized shoe-sole containing butadiene-styrene copolymers and graft copolymers of poly(butadiene) with styrene-acrylonitrile mixtures		117

U. S.	2,857,360	15.11.55	21.10.58	Rohm and Haas	Butadiene-*co*-styrene latex	Methyl methacrylate	Claims compositions of good impact strength when methyl methacrylate with or without additional monomer is polymerised with a free radical catalyst in the presence of a butadiene-styrene latex at 60°C over a period of 18 hr. Grafting is by transfer	*CA*, 53, 2686	118
Brit.	830,785	U. S. Appl. 15.11.55	23.3.60	Rohm and Haas	Equivalent to U. S. 2,857,360		See above	*CA*, 54, 12664	119
Brit.	824,263	24.11.55		Kodak	Polymer formed from polymerizing a *specified* monomer with a different monoethylenically unsaturated polymerizable compound containing a —CH=CH— group	Vinylidene chloride or vinyl chloride or a mixture thereof, together with another monoethylenically unsaturated polymerizable compound	Claims a process for preparing a graft polymer comprising polymerizing in a liquid medium from 95 to 5% of said monomer composition with from 5 to 95% of said copolymer; the latter may or may not be isolated from its polymerization medium		120
Brit.	824,920 divided out of Brit. 824,263	24.11.55					An example of the graft polymer may be vinyl chloride or vinylidene chloride and methacrylonitrile or acrylonitrile and methyl methacrylamide and/or *N*,*N*-dimethyl methacrylamide. Fibers or films with improved dyeability can be made from the graft polymers		121
Ital.	563,148	U. S. Appl. 1.12.55 1.5.56 29.11.56		Esso Research and Engineering	Poly(isobutylene) compound, e.g., copolymer of isobutylene-isoprene	Unsaturated organic ester	Claims on additive for lubricating oil obtained by exposing to high energy radiation a mixture of a poly(isobutylene) compound and a polymerizable monomer for a sufficient time to graft said monomer to said polymer compound		122

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	3,123,434	12.12.55	3.3.64	Du Pont	Acrylonitrile polymer or copolymer	Ethylenically unsaturated sulfonic acid or its salt	The antistatic properties of synthetic textile fibers, especially acrylonitrile fibers, are imporved by polymerizing an ethylenically unsaturated sulfonic acid or its salt in the presence of an acrylonitrile polymer or copolymer	*CA*, 60, 12174	123
U. S.	2,926,126	13.1.56		Rohm and Haas	Polyalkyl acrylate in which the alkyl portion contains no more than 18 carbon atoms	Specified monomer e.g., acrylonitrile, acrylic acid, styrene, vinyl ethers, etc.	Claims a method of preparing a graft copolymer of a polyalkyl acrylate with a specified monomer in which the polymer and monomer are exposed substantially simultaneously to 10^4–10^7 rads of high energy irradiation in the temperature range of −70 to +100°C		124
Brit.	855,711	U. S. Appl. 13.1.56		Rohm and Haas	Equivalent to U. S. 2,926,126		See above		125
Ital.	568,611	U. S. Appl. 13.1.56 11.1.57		Rohm and Haas	Equivalent to U. S. 2,926,126		See above		126
Brit.	825,882	U. S. Appl. 30.1.56	23.12.59	Phillips Petroleum	Liquid poly(butadiene)	Styrene	A mixture of titanium tetrachloride and triethyl aluminium or other similar catalyst combinations, is used to graft styrene onto a liquid poly(butadiene)	*CA*, 54, 11535	127
Brit.	866,069	14.2.56		T.I. (Group Services)	Poly(methyl methacrylate), poly(ethylene), poly(vinyl chloride)	Ethylene dimethacrylate, divinyl benzene, vinylidene chloride, lauryl methacrylate	A process for producing a polymer of improved properties which comprises mixing with a plasticizable polymer a compound compatible therewith which contains the polymerizable $>C=CH_2$ group and at		128

							least one other polymerisable olefinic double bond separated therefrom by at least one intervening carbon atom, and subjecting the resultant mixture to the action of ionising radiation. Also claims improving the properties of a polymer by subjecting it to the action of ionising radiation while in the presence of a polyfunctional monomer containing at least two potentially reactive carbon-carbon double bonds, one pair of carbon atoms joined by double bonds being separated from the pair by at least one carbon atom		
U. S.	2,861,974	17.2.56	25.11.58	Dow	Terpolymer of butadiene, styrene, and vinylidene chloride	Styrene	Styrene is grafted onto a terpolymer of butadiene, styrene, and vinylidene chloride by transfer initiated by benzoyl peroxide	*CA*, 53, 3757	129
Ital.	549,282	29.2.56		Polymer Corp.	Styrene-1,3-butadiene copolymer, an acrylonitrile-1,3-butadiene copolymer, poly-(styrene), or poly-(butadiene)	1,3 butadiene, styrene, acrylonitrile, butyl methacrylate, or methyl methacrylate	A graft copolymer of said constituents is formed by polymerizing the monomer in the presence of the previously oxidized polymer		130
Ital.	604,774	U. S. Appl. 5.3.56 8.3.56		Du Pont	(Process Claim)		Claims of process for modifying a polymeric structure wherein said polymer is contacted after irradiation, with one or more unsaturated homopolymerisable compounds. The temperature of the polymer is maintained at below room temperature, preferably below 0°C, during irradiation and the period of contact with said compounds		131

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Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
Brit.	819,049	U. S. Appl. 5.3.56		Dow	Poly(vinyl pyrrolidone), poly (vinyl alcohol), a copolymer of acrylonitrile and vinyl sulfonic acid, or a copolymer of vinylpyrrolidone and vinyl acetate	Acrylonitrile, or mixtures with other monoethylenically unsaturated monomers	A method for preparing graft copolymer containing fiber or film-forming systems which comprises dissolving in an aqueous poly(acrylonitrile) solvent saline solution, said monomer then polymerizing same in the presence of the dissolved polymeric material	132
Belg.	555,759	Ital. Appl. 14.3.56 13.3.57		Montecatini	Poly(propylene) or a propylene-ethylene copolymer	Vinyl or vinylidene compound, methyl methacrylate, methyl acrylate, styrene, butyl acrylate, or acrylic acid	A process for preparing grafted polymers comprises taking a shaped article made from said polymer which has been superficially peroxidized, contacting it with said monomer and polymerizing. Surface properties are thus modified easily and cheaply	133
Brit.	843,190	Ital. Appl. 14.3.56		Montecatini	Equivalent to Belg. 555,759		See above	134
Austral.	18,333/56	17.3.56		Centre National de la Recherche Scientifique	(Process Claim)		In the process for producing graft polymers, an improvement comprises subjecting a polymer to ionizing radiation while in contact with at least one vinyl compound of the group consisting of vinyl and divinyl monomers, said polymer being constituted of a monomer different from the group member used	135

Brit.	820,089	U. S. Appl. 27.3.56	General Electric	Poly(butadiene)	Vinyl aryl compound, e.g., styrene	Claims graft copolymers of butadiene and a vinyl aryl compound with poly(butadiene) linkages (comprising at least 30% 1-2-poly(butadiene)) prepared by heating a mixture of these two with dicumyl peroxide at 60–150°C and further heating the mixture at above 150°C	136
Belg.	556,134	U. S. Appl. 27.3.56 26.3.57	General Electric	Equivalent to Brit. 820,089		See above	137
Ital.	569,345	U. S. Appl. 27.3.56 23.3.57	General Electric	Equivalent to Brit. 820,089		See above	138
Brit.	816,024	U. S. Appl. 27.3.56 12.7.56	Du Pont	Polyester, polyamide, or polyether, poly(ethylene), poly(styrene), butadiene copolymers, PVC, P.T.F.E., P.F., U.F., and poly(acrylonitrile)	Chain transfer agents or telogens. Ethers, liquid and low melting hydrocarbons	Process for producing a coating on the surface of a shaped article of an organic polymer, which comprises the separate steps of exposing the surface of the shaped organic polymer, before the coating is applied, to action of ionizing radiation and while said surface is still activated applying to the surface in fluid form an organic compound which is chemically distinct from the polymer, non-polymerizable and fluid at a temperature below the softening temperature of the said organic polymer and so forming a coating which remains united to the polymer even when treated with solvents which normally dissolve said compound	139

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Belg.	556,633	U. S. Appl. 12.4.56 12.4.57		American Cyanamid	Polymeric organic reducing agent which is capable of being oxidized by a ceric salt, e.g., an alcohol, ketone, mercaptan, amine, aldehyde, or an acetal	Styrene, acrylonitrile, acrylamide, or methyl acrylate	Claims a process for preparing graft polymers by polymerizing a monomer containing a $CH_2{=}C<$ group in aqueous medium at a pH not greater than 6, in the presence of a ceric salt soluble in at least one constituent of the reaction medium and a polymeric reducing agent which can be oxidized by the ceric salt and which is thus capable of initiating the polymerization		140
Brit.	851,059	U. S. Appl. 12.4.56 14.12.56		American Cyanamid	Equivalent to Belg. 556,633		See above		141
Ital.	569,828	U. S. Appl. 12.4.56 14.12.56 2.4.57		American Cyanamid	Equivalent to Belg. 556,633		See above		142
Fr.	1,147,722	14.4.56	28.11.57	Saint-Gobain	Vinyl copolymers especially poly(vinyl chloride)	Vinyl monomers, e.g., acrylonitrile	Vinyl copolymers especially from PVC (I) with a high grafting rate and substantially improved physical, mechanical and physiochemical properties are prepared by subjecting I already grafted by swelling with a vinyl monomer and ionizing radiation, to one or more successive grafting operations by swelling and irradiation. The number of operations required to	*CA*, 54, 2819	143

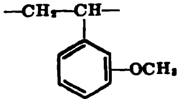
						obtain a certain grafting rate depends on the saturation of the polymer with the monomer, and this depends on the nature of the monomer, its swelling power for the polymer, degree of polymerization of the polymer, and the temperature	
Ger. (D.A.S.)	1,085,335	Fr. Appl. 14.4.56	Saint-Gobain	Equivalent to Fr. 1,147,722		See above	144
Belg.	556,649	Fr. Appl. 14.4.56 12.4.56	Saint-Gobain	Equivalent to Fr. 1,147,722		See above	145
Brit.	834,523 Addition to Brit. 819,049 (14.2.57.)	U. S. Appl. 23.4.56	Dow	Poly(vinylpyrrolidone)	Acrylonitrile, or its mixture with vinyl acetate, methyl acrylate, or vinyl pyridine	A method for preparing graft copolymer containing fiber- or film-forming compositions, which comprises dissolving in an organic poly(acrylonitrile) solvent consisting of dimethylsulfoxide, ethylene carbonate, or butyrolacetone, acrylonitrile alone or in admixture with another monomer soluble in the said organic solvent and a polymeric material, having a desired functional utility, which is soluble in the solution of the monomeric material in the organic solvent, then polymerizing the monomer in the presence of the dissolved polymer to form a graft copolymer containing the polymeric substance in spinnable dispersion	146

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Belg.	556,974	U. S. Appl. 25.4.56 19.2.57 25.4.57		O. W. Burke, Jr.	Hydrocarbon polymer, natural rubber, or a vinyl polymer	Monomer containing at least one ethylene and/or acetylenic bond	At least one monomer containing at least one ethylene and/or acetylenic bond is polymerized in the presence of a preformed polymer, there being used a heterogeneous organic metallic catalyst consisting of an organic metallic compound, and one or more constituents selected from a polar modifier, a Friedels Crafts compound and a vehicle		147
Brit.	821,971	U. S. Appl. 25.4.56 19.2.57 23.4.57	14.10.59	O. W. Burke, Jr.	Equivalent to Belg. 556,974		See above	*CA*, 55, 1088	148
Ger. (D.A.S.)	1,043,635	U. S. Appl. 30.4.56		Union Carbide	Poly(butadiene) and a copolymer of styrene-acrylonitrile	Styrene and acrylonitrile	Graft copolymers of styrene, and acrylonitrile are prepared by mixing styrene and acrylonitrile with an aqueous poly(butadiene) latex containing a styrene-acrylonitrile copolymer and heating in the presence of a free radical catalyst		149
Brit.	841,889	10.5.56	20.7.60	Borg-Warner	Diene rubber	Styrene and acrylonitrile	Styrene and acrylonitrile are copolymerized in the presence of a diene rubber to give a graft copolymer by transfer	*CA*, 55, 4055	150
U. S.	2,843,562	29.5.56		Eastman Kodak	Poly(vinyl alcohol), or a partially hydrolyzed poly(vinyl acetate)	Vinyl chloride (at least 80%) and a vinyl ester	The vinyl chloride monomer and a crosslinking agent selected from divinylbenzene, diallyl phthalate, triallyl phthalate, triallyl cyanurate, allyl acrylate, and ethylene glycol diacrylate, are combined by		151

						addition polymerization with the preformed polymer		
Belg.	558,004	Ital. Appl. 1.6.56 26.11.56 3.5.57 31.4.57	Montecatini	Poly(propylene) or a copolymer of propylene and ethylene	Ethylenically unsaturated monomer which contains in its molecule a group that is capable of increasing the infinity of polymer for acid or basic dyes or a group which can be converted into a group having these properties by quaternization with an organic base or by hydrolysis	Claims a shaped product obtained from a solid linear high polymer of propylene or a copolymer of propylene and ethylene onto which has been grafted polymer chains of said monomer		152
Brit.	850,471	Ital. Appl. 1.6.56 26.11.56 3.5.57	Montecatini	Equivalent to Belg. 558,004		See above		153
Brit.	832,567	U. S. Appl. 4.6.56	Rohm and Haas	Butadiene-styrene copolymer	Vinyl monomers	Vinyl monomers are polymerized in the presence of a butadiene-styrene latex using AZBN as the initiator to give grafting by transfer and the products blended with PVC to give high impact materials		154
U. S.	3,012,000	5.6.56	R. Aries	Copolymer of styrene and an alkyl methacrylate	Butadiene	Claims a graft copolymer of butadiene on a styrene-alkyl methacrylate copolymer. The reaction is initiated with $NaAlCl_4$	*CA*, 56, 8943	155

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	801,479	U. S. Appl. 5.6.56	17.9.58	Du Pont	Poly(ethylene terephthalate), poly(ethylene), or regenerated cellulose	Poly(ethylene oxide), poly (vinyl chloride), vinylidene chloride copolymer	A process for applying organic coatings (I) to a polymer substrate (II) without affecting the bulk physical properties of II comprises subjecting II in the presence of I to ionized charged particle radiation, preferably at room temperature. The energy of the beam must be more than sufficient to penetrate through the I to the surface of II in order to produce a chemical bond between II and I	*CA*, 53, 4815	156
Brit.	839,483	U. S. Appl. 5.6.56	29.6.60	Du Pont	Cellulose, poly(ethylene), nylon	Vinylidene chloride, acrylic acid, palmitic acid	Organic coatings are applied to polymers without affecting the physical properties of the polymer by a process which first exposes the substrate to ionizing charged particle radiation followed by treatment of the activated surface with a dissimilar organic coating material	*CA*, 55, 2183	157
U. S.	2,949,436	6.6.56		Polaroid Corp.	Specified polymer	Styrene	Claims graft copolymers prepared by polymerizing styrene in the presence of a polymer containing recurring groups of the formula  and a cationic polymerization catalyst		158

Brit.	860,408	U. S. Appl. 11.6.56	1.2.61	Du Pont	A normally solid linear polyamide, poly(vinyl halide), poly(vinyl acetal), halogenated or halosulfonated 1-alkene or polymers of vinyl compounds	Tetrafluoroethylene, hexafluoropropene, or perfluorocyclobutene	Claims a process for modifying said polymeric material which comprises irradiating the polymer under nitrogen while in contact with said monomer so that cross-links are created in the polymer at a faster rate than in the absence of added monomer	*CA*, 55, 17090	159
Ital.	573,532	U. S. Appl. 11.6.56 11.6.57		Du Pont	Equivalent to Brit. 860,408		See above		160
Brit.	823,462	14.6.56	11.11.59	Union Carbide	Ethylene homopolymers	Substances containing a single ethylenic unsaturation, e.g., vinyl acetate, vinyl chloride, acrylonitrile, methacrylonitrile, styrene, methacrylic acid, *N*-tertiary butylacrylonitrile, methyl methacrylate, or 2 ethyl hexyl acrylate	High energy or ionizing radiation is used to activate ethylene homo polymers. In this activated form, the poly(ethylene) is capable of producing graft polymers with polymerizable substances containing a single ethylenic unsaturation	*CA*, 54, 7237	161

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Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	852,042	Ital. Appl. 28.6.56		Montecatini	Substantially linear high mol wt homopolymer of an olefin of the general formula $CH_2=CHR$ wherein R represents an alkyl group, or a copolymer of two or more olefins of the general formula $CH_2=CHR^1$ wherein R^1 represents a H atom or an alkyl group	Vinyl chloride	Claims a graft copolymer of said constituents prepared by polymerizing vinyl chloride in the presence of said polymer and using as catalyst a peroxide, a redox system or a hydroperoxide of the polyolefin used		162
Ger. (D.A.S.)	1,065,618	Ital. Appl. 28.6.56	17.9.59	Montecatini	Equivalent to Brit. 852,042		See above	*CA*, 55, 17097	163
Brit.	872,513	U. S. Appl. 2.7.56 4.10.56 17.12.56		Du Pont	Synthetic condensation polymer, e.g., a polyamide	Monomers containing acid groups or acid salt groups other than carboxyl or carboxylate salt groups and possessing nonaromatic carbon-carbon unsaturation, e.g., styrene sulfonic acid	Claims a graft copolymer of said constituents		164

Brit.	872,514	U. S. Appl. 2.7.56 4.10.56 17.12.56	Du Pont	Linear condensation polyamides	Acidic polymerizable compound, e.g., acrylic or methacrylic acid.	Process for modifying said polymer which comprises incorporating in a shaped structure of the linear polyamide an acidic polymerisable compound containing aliphatic unsaturation and then effecting polymerization of said compound by heating the polyamide structure containing it under conditions such that the average chain length of the polyamide is substantially unchanged	165
Belg.	558,898 patent of improvement to Belg. 546,815 (6.4.56)	U. S. Appl. 2.7.56 4.10.56 17.12.56 2.1.57	Du Pont	Equivalent to Brit. 872,513 and 872,514		See above	166
Fr.	Addn. 72,111 addition to Fr. 1,149,298	U. S. Appl. 2.7.56 4.10.56	Du Pont	Equivalent to Brit. 872,513 and 873,514		See above	167
U. S.	2,959,569	5.7.56	Dow-Corning	Organopolysiloxane	Olefinic hydrocarbons, or halogenated olefinic hydrocarbons, e.g., styrene, vinyl acetate, acrylonitrile, acrylamide, acrylic acid, trifluorochloroethylene, etc.	A process for producing graft polymers which comprises homogeneously dispersing and suspending a finely divided inorganic solid throughout a mixture of said polymer and monomer and exposing the dispersion to the action of a free radical generator (e.g., ionizing radiation).	168

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	806,582	U. S. Appl. 5.7.56		Midland Silicones	Equivalent to U. S. 2,959,569		See above		169
Brit.	853,970 Addition to Brit. 809,838 (20.4.56)	Fr. Appl. 27.7.56		Centre National de la Recherche Scientifique	Poly(ethylene), poly(propylene), poly(vinyl chloride) polyamides, poly(glycol terephthalate), poly(styrene), rubber, cellulose, poly(methyl methacrylate)	Methyl methacrylate acrylonitrile, ethylene, vinyl chloride, vinyl carbazole butadiene (Process Claim)	Claims an improvement to the "pre-irradiation in air" method of forming graft copolymers wherein the grafted polymer is recovered while it still contains active centers and thereafter contacted with another monomer to form further grafted branches		170
Belg.	559,514	Fr. Appl. 27.7.56 24.7.57		Centre National de la Recherche Scientifique	Equivalent to Brit. 853,970		See above		171
Fr.	1,157,006	27.7.56	23.5.58	Centre National de la Recherche Scientifique	(Process Claim)		A process for producing graft polymers by subjecting a polymer to ionizing radiation and to contact with a monomer polymerizable by free radicals, wherein during said contacting of the polymer and monomer, the monomer is additionally contacted with a polymerizable inhibitor capable of substantially inhibiting homopolymerization thereof while maintaining said polymer on which the graft is being formed, substantially free from the action of said polymerization inhibitor	*CA*, 54, 20315	172

Brit.	853,971	Fr. Appl. 27.7.56	Centre National de la Recherche Scientifique	Equivalent to Fr. 1,157,006		See above	173
Belg.	559,515	Fr. Appl. 27.7.56 24.7.57	Centre National de la Recherche Scientifique	Equivalent to Fr. 1,157,006		See above	174
Ger. (D.A.S.)	1,056,829	Fr. Appl. 27.7.56	Centre National de la Recherche Scientifique	Equivalent to Fr. 1,157,006		See above	175
Brit.	821,000	Can. Appl. 14.8.56	Canadian Industries Ltd.	Polymer containing mercapto groups, e.g., a copolymer of a methacrylate —acrylic acid, poly(styrene) or styrene-glycidyl methacrylate converted into the acid chloride and reacted with β-mercapto ethanol	Ethylenically unsaturated monomer, e.g., ethyl acrylate, or methyl methacrylate	A process for the preparation of segmented polymers which comprises polymerizing an ethylenically unsaturated monomer in the presence of a polymer containing mercapto groups but free of groups inhibiting radical type polymerization of said monomer	176
Brit.	831,833	U. S. Appl. 14.8.56	Esso Research and Engineering	Butyl rubber latex	Vinyl acetate, acrylonitrile, or mixtures thereof	A process for the stabilization of a butyl rubber latex comprising admixing said latex with a specified polymerisable monomer and subjecting the admixture to 0.75–50 Mrad of high intensity ionising radiation	177

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
U. S.	2,873,240	22.8.56		American Cyanamid	Copolymer of α-chloroacrylonitrile with acrylamide, acrylonitrile, or methyl acrylate	Acrylic acid, acrylamide, styrene, or a substituted styrene or vinylpyridine	A specified monomer is polymerized in the presence of 0.1–5% α-chloroacrylonitrile; the resulting polymer is dissolved in a solvent together with chlorine and a dissimilar monomer (B.P. >60°C) containing a $CH_2{=}C<$ group. Free radicals are generated by photolyzing the solution	178
Brit.	833,585	U. S. Appl. 22.8.56		American Cyanamid	Equivalent to U. S. 2,873,240		See above	179
Ital.	578,224	U. S. Appl. 22.8.56		American Cyanamid	Equivalent to U. S. 2,873,240		See above	180
Ital.	558,040	23.8.56		Polymer Corp.	Water-soluble natural polymer, e.g., cellulose, gelatine, casein, pectin, alginates, carotene, and natural rubber latex	1,3-butadiene, styrene, acrylonitrile, methyl methacrylate, or acrylamide	Claims a process wherein a natural polymer is oxidized and then polymerized with a polymerizable compound. Oxidation is effected with a gas	181
Brit.	865,378	30.8.56		T. I. (Group Services)	Poly(vinyl chloride)	Nonvolatile unsaturated monomer, e.g., an allyl ester (diallysebacate or triallyl cyannurate)	A process for the manufacture of rigid or semirigid compositions based on vinyl chloride polymerization products, which comprises blending PVC and an essentially nonvolatile monomer having a plasticizing action on the polymer	182

						and then subjecting the resulting mixture to the action of ionizing radiation, whereby the monomer is converted to a polymeric form which has reduced plasticizing action on the polymer	
Ital.	577,772	U. S. Appl. 4.9.56 4.9.57	Houilleres	Poly(ethylene)	Ethylene	Claims a process for polymerizing at least one ethylenic monomer on the corresponding polymer by exposing the polymer to ionizing radiation in order to fix new polymer chains of the same quantitative composition to it	183
Brit.	856,884	21.9.56	G. Oster	High mol wt organic polymeric material eq., cellulose, nylon, paper or proteinaceous parchment, poly(acrylonitrile), poly(ethylene)	Ethylenically unsaturated monomer e.g., a vinyl or alkyl compound	A process for grafting synthetic polymers or high mol wt natural polymers, which comprises irradiating said polymer with UV light of λ 170–300 mμ for a time sufficient to form free radicals then containing the irradiated polymer with an ethylenically unsaturated monomer. There may be present during the irradiation an UV absorber of quantum yield between 10^{-2} and 1	184
Belg.	560,986	U. S. Appl. 21.9.56 20.9.57	G. Oster	Equivalent to Brit. 856,884		See above	185
Ital.	579,610	U. S. Appl. 21.9.56 7.9.57	G. Oster	Equivalent to Brit. 856,884		See above	186

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
Brit.	875,131 Addition to Brit. 820,120 (6.4.56)	U. S. Appl. 4.10.56		Du Pont	The polymers of styrene, the acrylic esters, vinyl chloride, vinyl fluoride, vinylidene chloride, vinyl acetate, the vinyl ketones, the vinyl ethers, the halogen, S, N, or P containing vinyls, the vinyl silanes, ethylene, propylene, tretafluoroethylene, alkyl esters, acrylonitrile, methacrylonitrile, and the diene rubbers	Monomer which contains reactive nonaromatic carbon-carbon unsaturation, and acid or acid salt groups or functional groups which can be and subsequently are converted to acid or acid salt groups	Process for the production of a grafted polymer in which the substrate is a synthetic addition polymer and the grafted structures at least in part contain free acid groups or acid salt groups, which comprises subjecting a substrate of said polymer to high energy radiation and contacting it simultaneously or subsequently while it is still in the activated state with said monomer for a time sufficient to produce the required grafted polymer	187
Ital.	600,849 Addition to Ital. 551,767	U. S. Appl. 4.10.56		Du Pont	Equivalent to Brit. 875,131		See above	188
Fr.	Addition 73,026 addition to Fr. 1,149,304	U. S. Appl. 4.10.56		Du Pont	Equivalent to Brit. 875,131		See above	189
	Addition 72,356							190

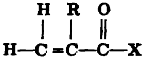
	addition to Fr. 1,149,305								
Belg.	553,374	Fr. Appl. 5.10.56	13.12.56	Chemstrand Corp.	Copolymer of 25–75% of a vinylpyridine and 75–25% of acrylic acid	Acrylonitrile 85% and up to 15% of another mono-olefinic monomer copolymerizable with acrylonitrile	The monomeric mixture is contacted with an aqueous solution of the preformed copolymer in the presence of a catalyst selected from water-soluble peroxy and azo catalysts, and heated until the monomeric compound has practically all polymerized		191
Ger.	1,111,828 (cf. Belg. 553,374 —see above)	11.10.56		Chemstrand Corp.	Copolymer of 25–75% of a vinylpyridine and 75–25% acrylic acid	Acrylonitrile (I) or mixtures containing at least 85% (I)	A graft copolymer of said constituents is prepared by a transfer method using a radical forming initiator. Such graft polymers, prepared without pH control, possess a high solubility in organic solvents, and are easily dyeable	*CA*, 56, 4973	192
Ital.	573,207	U. S. Appl. 15.10.56		Dow	Poly(ethylene), poly(propylene), or poly(styrene)	Acrylonitrile, vinylidene chloride or vinylpyrrolidone	Claims a process for contacting with ozone a specified polymer and subsequently contacting the treated polymer with a graft monomer capable of being polymerized by free radicals		193
Brit.	825,680	15.10.56	16.12.59	Dow	Addition polymers containing ethylenic unsaturation	Acrylonitrile, vinylidene chloride, or vinylpyrrolidone	Addition polymers containing ethylenic unsaturation are subjected to the action of air or oxygen containing 0.5–10% by vol. of O_2 at 0–40° and gauge pressure of from 0–30 lb/sq. in., and then brought into contact with the monomer to be grafted and heated with it under pressure to bring about the graft polymerization	*CA*, 54, 9361	194

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	2,956,899	18.10.56		Du Pont	Polyamide, or a polyester, e.g., poly(ethylene terephthalate)	Methyl acrylate	Claims a process which comprises (1) irradiating a shaped polymeric organic substrate in the presence of oxygen, (2) contacting the irradiation substrate with a chemically distinct unsaturated polymerisable monomer with no additional access of oxygen thereby polymerizing on and bonding it to the substrate, (3) removing excess monomer, and (4) recovering the graft polymer in the form of the original shaped substrate		195
Belg.	561,742	U. S. Appl. 18.10.56		Du Pont	Equivalent to U. S. 2,956,899		See above		196
Brit.	856,329 Addition to Brit. 801,531 (6.7.56)	U. S. Appl. 18.10.56		Du Pont	Equivalent to U. S. 2,956,899		See above		197
Fr.	1,160,106	26.10.56	8.7.58	Houilleres	Poly(ethylene)	Acrylonitrile and styrene or vinyl chloride and ethylene (Process Claim)	Claims a process in which a polymer is first activated by means of ionizing radiation and then grafted with at least two monomers in succession, the amount of the first monomer being less than the amount needed to exhaust the activity of the base polymer	*CA*, 54, 23446	198
Fr.	1,160,107	26.10.56	8.7.58	Houilleres	Poly(ethylene)	Mixture of styrene and acrylonitrile or ethylene and vinylidene	Claims a process for activating a polymer by ionizing radiation and reacting it with at least two mutually dissimilar monomers	*CA*, 54, 23446	199

						chloride (Process Claim)	simultaneously		
Fr.	1,160,108	26.10.56	8.7.58	Houilleres	Poly(tetrafluoroethylene), poly(styrene), poly(methyl methacrylate)	Tetrafluoroethylene styrene, methyl methacrylate	Claims graft copolymers produced by the reaction of a previously formed polymer or copolymer with the *corresponding* monomer(s) after or during irradiation of the original polymer	*CA*, 54, 23446	200
Brit.	866,131	Fr. Appl. 26.10.56		Houilleres	Equivalent to Fr. 1,160,107		See above		201
Brit.	872,537	Fr. Appl. 26.10.56		Houilleres	Equivalent to Fr. 1,160,106		See above		202
Ital.	578,962	Fr. Appl. 26.10.56		Houilleres	Equivalent to Fr. 1,160,106		See above		203
Ital.	579,214	Fr. Appl. 26.10.56		Houilleres	Equivalent to Fr. 1,160,107		See above		204
Can.	649,105	3.11.56	25.9.62	Polymer Corp.	Natural rubber, starch, cellulose, casein, etc.	1,3-Butadiene isoprene, styrene, methyl methacrylate, acrylonitrile, methacrylamide, vinyl ether, etc. (Process Claim)	A process is described for inhibiting homopolymer formation during graft polymerization of monomers with preformed polymers previously oxidized with oxygen and ozone. The addition of water-soluble reducing agents to a latex of a preformed polymer is suitable for destroying water soluble homopolymerization-initiated peroxy compounds. These include sodium formaldehyde-solfoxylate, formaldehyde, triethylenetetramine, and ferrous sulfate	*CA*, 58, 5853	205

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
Brit.	832,693	Can. Appl. 3.11.56		Polymer Corp.	Equivalent to Can. 649,105		See above	206
Ital.	579,759	Can. Appl. 3.11.56		Polymer Corp.	Equivalent to Can. 649,105		See above	207
U. S.	3,069,382	Can. Appl. 3.11.56		Polymer Corp.	Equivalent to Can. 649,105		See above	208
U. S.	2,970,129	15.11.56		Union Carbide Corp.	Poly(ethylene)	Compound of the general formula  $\mathrm{H{-}\overset{H}{\overset{\vert}{C}}{=}\overset{R}{\overset{\vert}{C}}{-}\overset{O}{\overset{\Vert}{C}}{-}X}$ wherein R is hydrogen or methyl and X is hydroxy or a lower alkyl-substituted amino group	Poly(ethylene) is dissolved in hydrocarbons or chlorinated hydrocarbons with said monomer in the presence of a free radical polymerization catalyst	209
U. S.	3,027,346	15.11.56		Union Carbide Corp.	Poly(ethylene)	Monomeric lower alkyl ester of acrylic acid or lower alkyl ester of methacrylic acid	Heating in contact with benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, acetyl peroxide, tertiary butyl hydroperoxide, tertiary butyl peroxide, lauroyl peroxide, peracetic acid, tertiary butyl permaleic acid or mixtures thereof, a preformed normally solid poly(ethylene), and said monomer, the	210

							poly(ethylene) being dissolved in an aromatic solvent, to form a homogeneous mixture comprising ethylene homopolymer, a second homopolymer of the carboxylic acid ester, and a graft copolymer of poly(ethylene) and the carboxylic acid ester		
Fr.	1,160,849	15.11.56	11.8.58	Saint-Gobain	Poly(vinyl chloride)	Acrylonitrile	Certain polymers can be mixed with PVC (I) if their respective monomers are first grafted to I. Thus, 0.80% poly(acrylonitrile) was mixed and heated with I that had been modified by grafting with 0–130% acrylonitrile (II). The modulus of rigidity and the bending temperature of the products depended approximately only on the total II added by grafting and mixing	*CA*, 54, 26009	211
Belg.	562,397	Fr. Appl. 15.11.56	14.11.57	Saint-Gobain	Equivalent to Fr. 1,160,849		See above		212
Brit.	822,751	21.11.56	28.10.59	Monsanto	Poly(styrene), or a copolymer of styrene-butadiene	Styrene, butadiene or a mixture of styrene and acrylonitrile	Graft copolymers are prepared by exposing to γ radiation (under nitrogen) an aqueous dispersion of an organic polymer and then introducing a monomer capable of radical addition polymerization	*CA*, 54, 10402	213
Ital.	580,942	Brit. Appl. 21.11.56		Monsanto	Equivalent to Brit. 822,751		See above		214

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Ital.	581,077	Fr. Appl. 24.11.56 31.1.57 2.2.57 14.6.57 23.11.57		Polyplastic	(Process Claim)		Claims preparation of substantially pure graft copolymers by ozonising a "Dry" polymer as defined to form labile functions, thus grafting the monomer onto the polymer. Ozonization may be effected while the polymer is being agitated in powdery form in a mixture, or during milling, or by dispersing the polymer in a liquid (containing the ozone-charged gas stream) which does not at once dissolve it		215
Brit.	883,791 Addition to Brit. 791,453	Fr. Appl. 24.11.56 31.1.57 2.2.57 14.6.57	6.12.61	Polyplastic	Equivalent to Ital. 581,077		See above	*CA*, 57, 3637	216
Brit.	883,792	Fr. Appl. 24.11.56 31.1.57		Polyplastic	Poly(ethylene)	An acid containing a vinyl group, e.g., acrylic acid	Claims a graft copolymer consisting of a backbone of poly(ethylene) and up to 52% by wt of an acid containing a vinyl group, prepared by heating the acid in vacuo with a preozonized sample of the polymer	*CA*, 57, 3637	217
Brit.	883,793	Fr. Appl. 24.11.56		Polyplastic	Poly(propylene)	Vinylpyridine or vinyl carbazole	Resinous articles are prepared from poly(propylene) by grafting vinylpyridine or vinyl carbazole onto it using the method as described above	*CA*, 57, 3637	218

Ger.	1,133,891	Fr. Appl. 24.11.56 31.1.57 2.2.57	26.7.62	Polyplastic	Equivalent to Ital. 581,077		See above	*CA*, 57, 14001	219
Belg.	562,661	Fr. Appl. 24.11.56 2.2.57 14.6.57		Polyplastic	Equivalent to Ital. 581,077		See above		220
Ital.	578,721	26.11.56	1.7.58	Montecatini	Poly(propylene)	Vinylpiperidine, vinyl quinoline, vinylpyrrolidone, or vinyl carbazole	Claims the use, in graft polymerization on manufactured articles made from linear high polymers of propylene, of a vinyl monomer containing one or more basic groups in the molecule. Another monomer may also be used as well as the basic monomer, this being chosen from alkyl acrylates and methacrylates or acrylonitrile		221
Brit.	824,368	28.11.56	25.11.59	Styrene Products Ltd.	Poly(styrene) and a butadiene-styrene copolymer	Divinylbenzene and ditertiary butyl diperphthalate	Poly(styrene) is milled with a butadienestyrene copolymer together with divinyl benzene and ditertiary butyl diperphthalate to give a complex graft copolymer of the high impact resistant type	*CA*, 55, 2194	222
Fr.	1,210,632	11.12.56		Houilleres	Poly(ethylene)	Vinyl acetate	Claims products suitable for forming films and coatings, such as paints, varnishes, mastics, textile, and other coatings, made by grafting vinyl acetate chains onto polythene		223

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	869,180	U. S. Appl. 13.12.56		Dow	Poly(vinylpyrrolidone)	Monoethylenically unsaturated acrylonitrile containing material	Claims a spinnable, fiber-forming composition comprising an acrylonitrile polymer or copolymer and a graft copolymer of said constituents dispersed in an aqueous organic solvent comprising water-containing ethylene carbonate, dimethyl sulfoxide or butyrol acetone		224
Fr.	1,164,023	27.12.56	6.10.58	Pechiney-Compagnie de Products Chimiques et Electrometallurgiques	Poly(vinyl chloride)	Styrene, acrylonitrile, methyl methacrylate, vinyl stearate, and acrylamide	A homogeneous, air-free mixture of a polymer and a monomer is prepared by degassing a pulverized suspension of the polymer, adding the desired amount of monomer, and agitating the mixture until the monomer is absorbed. Irradiation of the resultant suspension (with x-rays) yields a homogeneous graft copolymer.	*CA*, 54, 25974	225
					Poly(ethylene)	Styrene, acrylonitrile	Also claims adding a degassed aqueous suspension of PE, the PE having first being irradiated in air		
U. S.	2,908,661	11.1.57	13.10.59	Borg-Warner	Poly(butadiene) latex	Mixture of α-methylstyrene and acrylonitrile	Acrylonitrile and styrene or α-methyl styrene are polymerized in butadiene latex to give a graft copolymer by transfer	*CA*, 54, 1934	226
U. S.	2,908,662	22.1.57		Shawinigan Chemicals	Poly(vinyl chloride) or a vinyl chloride copolymer	Alkyl ester of acrylic acid	An unsaturated polymer is prepared by reacting a solution of said polymer with up to 20% vinyl acetate, in dioxane or D.M.F. with ammonia at 20–150°C and 40–100		227

							psig whereby HCl is removed. The unsaturated polymer is recovered from solution and reacted with said monomer in the presence of an organic peroxygen compound as polymerization catalyst		
Brit.	862,610	25.1.57	15.3.61	B.X. Plastics	Cellulose triacetate	Styrene	Cellulose triacetate is subject to ionizing radiation such as x-rays in the presence of oxygen or air to form peroxidized active centers, and the irradiated material is then treated with styrene	*CA*, 57, 2436	228
Brit.	870,052	25.1.57		B. X. Plastics	Cellulose triacetate	Styrene	Cellulose triacetate is mixed with styrene and irradiated *in vacuo* at room temperature to form a graft copolymer	*CA*, 56, 8942	229
Brit.	829,512	U. S. Appl. 31.1.57 9.12.57	2.3.60	Dow	Copolymer of vinyl chloride and vinyl acetate	Ethylene glycol dimethacrylate	Vinyl chloride polymers, after forming, are crosslinked by graft copolymerization with polyfunctional monomers under exposure to high energy radiation	*CA*, 54, 17967	230
Ger.	1,099,170	Fr. Appl. 2.2.57 25.11.57		Polyplastic	Poly(styrene)	Acrylonitrile	The monomers are polymerized in the presence of ozonized polymers in which case the monomers graft on the ozonized polymers and form graft copolymers which remain soluble in the low boiling solvent	*CA*, 56, 2589	231
Brit.	863,211	13.2.57	22.3.61	B. X. Plastics	Poly(ethylene) or cellulose triacetate (Process Claim)	Acrylonitrile or styrene	In the formation of graft copolymers by using ionizing radiation to form active centers on the polymer chain, the formation of unwanted homopolymers may be diminished by maintaining the grafting material in the vapor phase	*CA*, 55, 18198	232

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Belg.	564,910	19.2.57 4.10.57		Montecatini	Poly(propylene)	Styrene, divinylbenzene or an ester, a halide or an amine of maleic, fumaric or acrylic acid	A process for preparing a polymer composition having a high affinity for coloring agents, by mixing poly(propylene) with at least one monomer and then heating at a temperature above the mp of the poly(propylene) so that the said monomer is graft copolymerized onto the polymer backbone		233
Brit.	875,758	Ital. Appl. 19.2.57 4.10.57 14.2.58		Montecatini	Equivalent to Belg. 564,910		See above	*CA*, 56, 4971	234
U. S.	2,913,426	20.2.57	17.11.59	Catalin Corp. of America	Styrene-butadiene rubbers	Styrene and vinyl toluene	Styrene and vinyl toluene are copolymerized in suspension in the presence of an SBR using an azo and a peroxide initiator to give grafting by transfer	*CA*, 54, 4047	235
Japan	646('59)	2.3.57		Haris Kabushiki Kaisha	Poly(isobutylene)	Vinyl acetate	A process for the production of low mol wt graft copolymers from said constituents in which the vinyl acetate is grafted with poly(isobutylene) by heating and agitating in the presence of an aliphatic ketone containing alkyl radicals having 1 to 4 C atoms, and an organic peroxide catalyst. The copolymers may be used as a base for chewing gum	*CA*, 54, 7230	236

Brit.	834,954	Japan Appl. 2.3.57		Haris Kabushiki Kaisha	Equivalent to Japan 646(59)		See above		237
Germ. (D.A.S)	1,084,026	Japan Appl. 2.3.57		Haris Kabushiki Kaisha	Equivalent to Japan 646(59)		See above		238
Germ.	1,086,047 Addition to Germ. 1,070,825 (see Brit. 809,836)		28.7.60	Centre Nationale de la Recherche Scientifique	Poly(ethylene)	(Process Claim)	The polymer is irradiated in the presence of oxygen and subsequently grafted with a monomer in the absence of oxygen, possibly at higher temperatures. Repeated grafting with different monomers is possible if the activated backbone is brought into contact with the single monomer at different temperatures. Alternatively, the grafting is performed at a suitable temperature by regulating the contact time with the single monomer	*CA*, **55**, 24116	239
Germ.	1,103,568	7.3.57		Metall-Gesellschaft	Natural or synthetic rubber	Monomers containing tertiary nitrogen atoms	Rubber has its resistance to oil or solvent increased by grafting said monomers onto the main chain and treating the product with alkyl halides and/or dialkyl sulfates, and/or alkaryl sulfonates and if necessary subsequent vulcanization		240
Brit.	858,776	U. S. Appl. 11.3.57		Union Carbide Corp.	Copolymer of butadiene and styrene	Mixture of styrene and acrylonitrile	Claims a composition having improved physical and processing qualities, which comprises a mixture of a vinyl chloride homo- or copolymer and a graft copolymer of styrene and acrylonitrile onto a butadiene-styrene rubber		241

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	847,602	19.3.57		Monsanto	Poly(styrene) or SBR	Butadiene or acrylonitrile	A process for the preparation of a graft polymer in which an aqueous dispersion of a polymer or copolymer obtained by emulsion polymerization of a vinyl compound is treated with a chemical polymerization catalyst *in vacuo* such that active centers are induced in the trunk of the polymer and a monomer capable of radical addition polymerization is then introduced to graft polymerize directly onto the active centres		242
Ital.	587,599	Brit. Appl. 19.3.57		Monsanto	Equivalent to Brit. 847,602		See above		243
Belg.	565,853	Brit. Appl. 19.3.57		Monsanto	Equivalent to Brit. 847,602		See above		244
Brit.	847,603 Addition to Brit. 847,602	19.3.57		Monsanto			Process as in Brit. 847,602 except that a redox polymerization catalyst is used to induce the active centres on the backbone polymer		245
Ital.	586,488	Fr. Appl. 27.3.57		Ethylene Plastique	Poly(ethylene)	Specified monomers	Claims graft copolymers of 95–5% ethylene with a monomer or monomers where Young's modulus is reduced to the same value as that required for the final graft copolymer or less		246
Brit.	840,070	U.S. Appl. 29.3.57	6.7.60	Esso Research and Engineering	Poly(ethylene)	Divinylbenzene	A low temperature, low pressure polyethylene is grafted by irradiation in contact with divinylbenzene using Co^{60} at 25°C	*CA*, 55, 1084	247

U. S.	2,862,906	1.4.57	2.12.58	Monsanto	A mixture of an interpolymer of an acrylic acid with an acrylate and a bis(sulfoaryl) alkane	Vinyl aromatic hydrocarbon monomers	Granular polymerization products are prepared from an aqueous dispersion of a vinyl aromatic hydrocarbon monomer, a ring halogenated vinyl aromatic hydrocarbon, or their mixture in the presence of a dispersion agent. The latter consists of a mixture of water soluble interpolymer of an acid monomer of acrylic acid, methacrylic acid or their mixture with 2-ethyl hexyl acrylate, 2-ethyl hexyl methacrylate, or their mixture and a bis(sulfoaryl)alkane or water-soluble salt thereof	*CA*, 53, 7663	248
U. S.	2,862,907	1.4.57	2.12.58	Monsanto	Rubbery conjugated 1,3-diene polymer	Vinyl monomers	Granular polymerization products are prepared by agitating and heating a mixture of water and a partially polymerised solution of a rubbery conjugated 1,3-diene polymer in a vinyl monomer to ⩾ 100°C in absence of a dispersing agent. Then the dispersion agent described above is added. The mixture is agitated and heated until the polymerization is complete	*CA*, 53, 7664	249
Fr.	1,210,637	9.4.57		L. Adany	Paraffinic hydrocarbon which may contain as impurity up to 20% of unsaturated hydrocarbons	Vinyl monomer	Claims a process for the radiation grafting of at least one polymerizable vinyl monomer mixed with a supporting material consisting of at least one paraffin hydrocarbon. The vinyl monomer is dissolved in the hydrocarbon and heated, the solution is cooled slowly to form a stable homogeneous gel, and then exposed to ionising radiation		250

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Fr.	Addn. 73,448 Addition to Fr. 1,172,070	Ital. Appl. 9.4.57		Montecatini	Partially crystalline polymer consisting of either an isotactic polymer or a polymer containing isotactic structural units derived from one or more α-olefins of formula $CH_2=CHR$ where R is an alkyl group	Vinylbenzene monomer preferably styrene	A vinylbenzene compound is polymerised at 70–130°C in the presence of said polymer this polymer being insoluble, at least in the hot, in the monomeric vinylbenzene compound		251
Ger.	1,120,126	11.4.57		Metallgesellschaft	Prevulcanized natural or synthetic rubber latex to which amine-activated peroxide catalysts may be added	Organic compounds containing ethylene groups and a basic tertiary N atom, e.g., vinylpyridine, and vinylquinoline and their alkylated derivatives, and (meth)acrylate esters of tertiary aliphatic amino alcohols	Claims a process for copolymerizing said organic compounds with natural or synthetic rubber latex. 5–30% based on the dry weight of the end product, of the organic compound is added in stages to the latex so that the solubility limit of the compound in the aqueous phase of the reaction mixture is not exceeded and the aqueous phase of the mixture forms not less than 70%		252
Fr.	1,171,805	19.4.57	30.1.59	Societe Nobel Francaise	Cellulose	Polymerizable monomer, e.g., styrene, vinyl acetate	Cellulosic graft copolymers are obtained by subjecting to the action of ionising rays a mixture of at least one cellulosic derivative and at least one polymerizable monomer. Previous to the irradiation, air may be eliminated from the mixture by mechanical action such	*CA*, 54, 26017	253

							as extrusion or compression. The fusion temperature of the resulting graft copolymers is controlled by varying the ratio of cellulosic polymer to monomer and by the use of chain transfer agents during polymerization		
Fr.	1,171,806	19.4.57	30.1.59	Societe Nobel Francaise	Cellulose	Vinyl acetate	The addition of 10^{-6} to 3×10^{-2} parts hexahydro-1,3,5-triacryloyl-s-triazine (I) per part of the polymerization mixture makes it possible to decrease the amount of irradiation necessary to prepare graft copolymers of cellulose and vinyl acetate. Concentrations of I from 10^{-6} to 10^{-3} tended to accelerate the polymerization, while concentrations of 10^{-3} to 3×10^{-2} tended to cause crosslinking	*CA*, 54, 26017	254
Belg.	566,903	Fr. Appl 19.4.57		Nobel-Bozel	Equivalent to Fr. 1,171,805		See above		255
Brit.	860,244	Fr. Appl. 19.4.57		Nobel-Bozel	Equivalent to Fr. 1,171,805		See above		256
U. S.	2,965,571	30.4.57		Standard Oil Co.	Copolymer of propylene or isobutylene with styrene, isopropylstyrene, or isopropyl methylstyrene	Specified acrylic monomer	Claims a composition comprising a hydrocarbon lubricating oil and a small proportion of a graft copolymer of said constituents having a molar ratio of acrylic monomer to aromatic compound to alkene from 1:1:1 to 50:1:50 and having a mol wt 20,000 to 150,000. The grafting reaction is initiated by hydroperoxidizing the backbone polymer and reacting it with said acrylic monomer		257

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
U. S.	2,965,572	30.4.57		Standard Oil Co.			Composition as above except that the backbone copolymer is claimed as that formed from polymerizing styrene, isopropyl styrene, or isopropyl methyl styrene with an alkyl acrylate or methacrylate wherein the alkyl groups contain at least 4 C atoms	258
Ital.	591,490 Second patent of addition to Ital. 565,618	3.5.57		Montecatini	Poly(propylene)	Monomers containing reactive acid or basic groups	Claims an improvement to the process for preparing products containing grafted poly(propylene) polymers as in the principal patent, in that the grafted monomers contain reactive acid or basic groups thus giving the products particular affinity for basic or acidic dyes, respectively	259
Austrl.	49,301/59	3.5.57		Montecatini	Poly(propylene)	Amino alkyl methacrylate	Claims a resinous article comprising a linear high polymer of propylene having grafted thereon a polymer of an amino alkyl methacrylate	260
U. S.	2,905,653 Divided out of U .S. Appl. 372,390 4.8.53 which is a con-	14.5.57		Firestone Tire and Rubber Co.	Poly(acrylonitrile)	Vinyl ester	Claims a graft copolymer prepared by polymerizing a vinyl ester of a C_{1-8} carboxylic acid in an aqueous emulsion of an acrylonitrile homopolymer, said copolymer containing 10–25% of combined vinyl ester	261

	tinuation of Appl. 304,213 13.8.52								
U. S.	3.101.275	15.5.57		Du Pont	Nylon or poly(ethylene terephthalate)	Polymerizable monomer (Process Claim)	The fixing of a coating such as an antistatic film to a polymer film by the use of ionizing radiation is described. The substrate is first swollen by the addition of an appropriate liquid, and after irradiation, at least half the swelling liquid is removed from the polymeric substrate without affecting the superimposed film		262
Ital.	586,489	Fr. Appl. 23.5.57		Ethylene-Plastique	Poly(vinyl chloride) and/or poly(isobutylene) and/or poly(vinyl acetate)	Ethylene	Claims a process for obtaining graft copolymers by exposing to (unspecified) grafting conditions a mixture of at least one polymer product and ethylene, the proportion of said polymer being at most 95%, where the Young's modulus of the final graft copolymer may be adjusted by regulating that of the initial polymer		263
Brit.	884,732	Fr. Appl. 23.5.57	13.12.61	Ethylene-Plastique	Poly(vinyl chloride) or poly(vinyl acetate)	Ethylene	Graft polymers are prepared containing ethylene and a plasticizer which have tensile properties of high mol wt poly(ethylene). Thus, powdered PVC is preirradiated in air and then heated with ethylene in the absence of air to form a graft copolymer, to which is then added 25% dibutyl phthalate	*CA*, 57, 1089	264

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
U. S.	2,955,015	5.6.57		American Cyanamid	Paper substrate composed predominantly of cellulose fibers	Ethyl acrylate, propyl acrylate, or butyl acrylate	A paper substrate composed predominantly of cellulose fibers is reacted with said monomer in an aqueous medium at a pH not greater than 3.5 in the presence of a ceric salt which is soluble in at least one component of the reaction medium until the weight of the said acrylate combined with said substrate is between 100 and 900% based on the weight of the substrate	265
U. S.	3,101,276	8.7.57		Du Pont	Cellulose	Vinyl monomers, e.g., vinyl acetate acrylonitrile or glycidyl methacrylate	In a process for grafting a polymer onto a cellulose substrate using ionising radiation, an ethylenically unsaturated monomer is brought into contact with the substrate and is polymerised *in situ*. By the use of an agent to cause swelling, the efficiency of utilisation of the radiation is improved. The swelling agent may be water or an aqueous solution such as dilute mineral acid, caustic alkali, or a metallic salt	266
Brit.	845,690	U. S. Appl. 8.7.57		Du Pont	Equivalent to U. S. 3,101,276		See above	267
Belg.	569,421	8.7.57		Du Pont	Equivalent to U. S. 3,101, 276		See above	268
Ital.	592,251	8.7.57		Du Pont	Equivalent to U. S. 3,101,276		See above	269
Brit.	888,231	8.7.57		Rubber and Plastics Research	Poly(vinyl chloride)	Chloroprene	A process for preparing polymeric and vulcanizable products comprising grafting molecules of PVC	270

				Association of Great Britain			with molecules of polychloroprenes which have been prepared by polymerizing chloroprene in such a way that neither sulfur nor its compounds are attached to the poly(chloroprene) chain. The polymer constituents are grafted by mechanical mastication in the presence of oxygen to produce an interpolymer		
U. S.	2,927,093	2.8.57	1.3.60	Goodyear Tire and Rubber Co.	Copolymer of styrene-acrylonitrile	Butadiene	Claims a blend consisting of a vinyl chloride resin, a copolymer of butadiene-acrylonitrile and a graft polymer of said constituents. The latter is prepared by polymerizing butadiene in the presence of a poly(styrene-acrylonitrile) latex. The composition may be used as an improved automotive crash-pad sheeting	*CA*, 54, 13711	271
Brit.	841,744	U. S. Appl. 2.8.57	20.7.60	Goodyear Tire and Rubber Co.	Equivalent to U. S. 2,927,093		See above	*CA*, 54, 25937	272
U. S.	2,927,095	2.8.57	1.3.60	United States Rubber Co.	Poly(butadiene)	Mixture of an aryl monomer such as styrene, α-methyl styrene the nuclear substituted monomethylstyrenes and an acidic monomer of a methacrylic acid, cinnamic acid, acrylic acid, or their mixtures	A high impact resistant material is prepared by mixing a copolymer of styrene and methacrylic acid with a poly(butadiene) grafted with the same monomers. Grafting is effected in the latex phase by transfer	*CA*, 54, 16028	273

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	839,069	U. S. Appl. 2.8.57	1.3.60	United States Rubber Co.	Equivalent to U. S. 2,927,095		See above	*CA*, 54, 16028	274
Belg.	569,890	U. S. Appl 2.8.57		United States Rubber Co.	Equivalent to U. S. 2,927,095		See above		275
U. S.	2,998,329	5.8.57		Dow	Cellulose substrates	Water soluble ethylenically unsaturated monomer that is polymerizable in aqueous solution under the influence of a field of ionizing radiation	Method for modifying pure cellulosic substrates which comprises partially swelling said substrate in an aqueous solution of monomer at neutral pH and exposing the mixture to a field of ionizing radiation until at least the surface of the substrate has been modified by grafted polymer		276
Belg.	569,852	Fr. Appl. 7.8.57		Nobel-Bozel	Poly(vinyl), poly(acrylic), poly(styrene) or cellulosic type (Processs claim)	Polymerizable monomer	A process for modifying the properties of high polymers by adding to a fine particle dispersion of a high polymer in water at least one polymerizable monomer until a homogeneous emulsion or suspension is obtained, and then submitting this mixture to the action of ionizing radiations so as to cause at least partial grafting		277
Brit.	883,473	Fr. Appl. 7.8.57		Nobel-Bozel	Equivalent to Belg. 569,852		See above	*CA*, 57, 1093	278

Brit.	871,572	23.8.57	28.6.61	B. X. Plastics	Poly(ethylene)	Acrylonitrile (Process Claim)	Graft copolymers with the production of less homopolymer in the monomer phase are prepared by leaching peroxide material from the polymer which has been irradiated in the presence of oxygen to produce active centers. The irradiated leached polymer is then treated with grafting monomers. The organic solvent used for the leaching, e.g., CH_2Cl_2 or acetone, is a nonsolvent for the base polymer	*CA*, 55, 25373	279
Fr.	1,214,892	Brit. Appl. 23.8.57		B. X. Plastics	Equivalent to Brit. 871,572		See above		280
U. S.	3,081,242	Brit. Appl. 23.8.57		B. X. Plastics	Equivalent to Brit. 871,572		See above		281
Brit.	901,997	U.S. Appl. 28.8.57		Foster-Grant	Natural rubber, poly(chloroprene), or an acrylonitrile butadiene copolymer	Styrene	A method of producing an interpolymer which method comprises flowing an interpolymerizable solution of styrene and a rubbery polymer through an elongated tubular chamber and subjecting the solution in its passage through the chamber to such increasingly higher polymerizing temperatures as to effect a progressive interpolymerization of the constituents of the solution. The apparatus used in this method is also claimed		282

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Fr.	1,181,893	2.9.57	19.6.59	Rhone-Poulenc	Poly(ethylene terephthalate), poly(vinyl alcohol) cellulose acetate (Process Claim)	Vinyl acetate, acrylonitrile, vinyl acetate	A polymer or shaped article of polymeric material is surrounded by monomer in gaseous or vapor form and submitted to ionizing radiation. If thick, the article is first softened by immersion in a solvent. Conditions of temperature and pressure are adjusted to avoid condensation or polymerization of the monomer	*CA*, 54, 26017	283
Brit.	850,446	Fr. Appl. 2.9.57 18.11.57		Rhone-Poulenc	Equivalent to Fr. 1,181,893		See above		284
Belg.	570,822	Fr. Appl. 2.9.57 18.11.57		Rhone-Poulenc	Equivalent to Fr. 1,181,893		See above		285
U. S.	3,107,206	Fr. Appl. 2.9.57		Rhone-Poulenc	Equivalent to Fr. 1,181,893		See above		286
Brit.	844,791	4.9.57	17.8.60	Natural Rubber Products Research Association and United Kingdom Atomic Energy Authority	Natural rubber	Vinyl monomers, e.g., methyl methacrylate	A stabilized natural rubber latex containing a polymerizable vinyl monomer is subjected to high energy irradiation at room temperature to form a graft copolymer	*CA*, 55, 5007	287

Brit.	861,454	4.9.57	22.2.61	B. X. Plastics	Copolymer of vinyl chloride and vinylidene chloride	Acrylonitrile	An unplasticized sheet of said copolymer (I) containing 0.5% stearic acid is soaked in acrylonitrile for 10 hr and then irradiated *in vacuo* with γ-rays from Co^{60}. The clear film produced is partially crosslinked, much harder, and has a higher softening temperature than (I). The polymerization is marked by its rapidity and use of low doses of irradiation	*CA*, 55, 17102	288
Brit.	861,455	4.9.57	22.2.61	B. X. Plastics	Copolymer of vinyl chloride and vinylidene chloride	Ethyl acrylate	An analogous process as above using ethyl acrylate monomer instead of acrylonitrile yields a modified film similar to conventionally (e.g., in dioctyl phthalate) plasticized I without the drawback of plasticizer migration or leaching with solvents	*CA*, 55, 17102	289
U. S.	3,066,085	Brit. Appl. 4.9.57		B. X. Plastics	Equivalent to Brit. 861,454		See above		290
U. S.	3,121,672	Brit. Appl. 4.9.57		B. X. Plastics	Equivalent to Brit. 861,455		See above		291
Belg.	568,423	13.9.57		Dow	Poly(acrylonitrile)	*N*-vinyl lactam, e.g., *N*-vinylpyrrolidone	Process for improving the dye-affinity of acrylonitrile polymers by incorporating *N*-vinyl lactam in an aquagel of the acrylonitrile polymer and subjecting to high energy radiation to form a graft polymer		292

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	837,334	9.10.57	9.6.60	Distillers	Poly(styrene)	Chloroprene	Chloroprene is polymerized by a free-radical catalyst in the presence of poly(styrene) latex to give a graft copolymer by transfer. The grafted polymer has good clarity and high impact strength	*CA*, 54, 26013	293
Brit.	837,335	9.10.57	9.6.60	Distillers	Poly(chloroprene)	Styrene	Styrene is polymerized by a freeradical catalyst in the presence of poly(chloroprene) to give a graft copolymer by transfer	*CA*, 54, 26013	294
Fr.	1,217,675	Brit. Appl. 9.10.57		Distillers	Equivalent to Brit. 837,335		See above		295
Belg.	572,125	Fr. Appl. 18.10.57 31.10.57		Polyplastic	(Process claim)		Process of preparing graft copolymers in which a previously ozonized polymer is contacted with the vapor of a monomer polymerizable by a free radical mechanism, the vapor base being free from polymerization inhibitors, especially air. Also claims a process in which polymer films are ozonized continuously, then passed into a chamber full of grafting monomer		296
Brit.	898,709	Fr. Appl. 18.10.57		Polyplastic	Equivalent to Belg. 572,125		See above		297
Belg.	572,100	Fr. Appl.		Centre National	Polyolefin, halogenated polyole-	Isoprene, styrene; or methyl	Graft copolymers are obtained by subjecting a supporting polymer to		298

		26.10.57 31.1.58 12.2.58		de la Recherche Scientifique	fin, poly(tetrafluoroethylene), poly(trichlorofluoroethylene), or a polymer containing no H atoms	methacrylate	ionizing radiation in the presence of a grafting monomer, the polymer being such that it is not easily penetrated by the monomer, and operating conditions being arranged so that the rate of polymerization of the monomer is lower than the rate of penetration of the monomer in the course of grafting. The monomer may be dissolved in a solvent, such as benzene and the intensity of the radiation may be varied during the course of the reaction		
Brit.	883,728	Fr. Appl. 26.10.57 31.1.58 12.2.58	6.12.61	Centre National de la Recherche Scientifique	Equivalent to Belg. 572,100		See above	*CA*, 57, 1089	299
Austrl.	42,739/58	Fr. Appl. 26.10.57 31.1.58 12.2.58		Centre National de la Recherche Scientifique	Equivalent to Belg. 572,100		See above		300
Fr.	1,334,305	31,10.57	9.8.63	Ethylene-Plastique	Poly(ethylene) or a condensation polymer made from phthalic and maleic acids (Process claim)	Vinyl acetate or styrene	Irradiation of a polymer as a melt or in solution followed by monomer addition and grafting results in a more uniform product and easier processing	*CA*, 60, 3167	301

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
Brit.	894,395	U. S. Appl. 31.10.57		Du Pont	Synthetic condensation polymer having recurring oxygen or sulfur atoms as the sole hetero- atoms in the chain, e.g., poly(ethylene terephthalate), polyoxymethylenes, polyacetals, and polycarbonates	Aliphatically unsaturated compound containing an amide group (or a polymer of such an unsaturated compound), e.g., acrylamide or *N*-vinylpyrrolidone	Claims a process for the production of graft copolymers of said constituents wherein the condensation polymer is chemically modified by producing free radicals thereon by means of high energy ionizing radiation while the polymer is in contact with said monomer	302
Belg.	572,578	U. S. Appl. 31.10.57		Du Pont	Equivalent to Brit. 894,395		See above	303
Brit.	898,710 Divided out of Brit. 898,709 (18.10.57)	Fr. Appl. 31.10.57		Polyplastic			Claims an apparatus for graft copolymerization of a polymer in the form of a finished or semifinished article of continuous elongated character, such as film, wire or sheet, which has previously been subjected to an activating process	304
Brit.	901,038	U. S. Appl. 31.10.57 13.10.58		Du Pont	Condensation polymer, e.g., poly(hexamethylene adipamide) or a poly(caproamide)	*N*-vinylpyrrolidone, *N*-methyl, *N*-vinyl formamide, acrylamide or methacrylamide	Claims graft copolymers of high mol wt synthetic nitrogenous condensation polymers in which the grafted units are linear side chains without aliphatic unsaturation, carry amide groups and are linked to the polymers by carbon-carbon bonds	305
Belg.	572,577	U. S. Appl.		Du Pont	Equivalent to Brit. 901,038		See above	306

		31.10.57 13.10.58					
Brit.	901,039	U. S. Appl. 31.10.57	Du Pont	Wool, cotton, poly(ethylene terephthalate), poly(hexamethylene adipamide), acrylonitrile homo- or copolymers	Vinyl pyridine, *N*-vinylpyrrolidone, acrylic acid, acrylamide, or derviatives of these compounds	Claims a graft polymer in which the side chains are grafted to the polymeric substrate by carbon-carbon bonds and contains biologically active groups	307
Ital.	608,998	U. S. Appl. 31.10.57	Du Pont	Equivalent to Brit. 901,039		See above	308
Belg.	572,579	31.10.57	Du Pont	Equivalent to Brit. 901,039		See above	309
Belg.	572,906	Fr. Appl. 16.11.57	Rhone Poulenc	(Process claim)		Making shaped articles of graft copolymers by impregnating a shaped or unshaped trunk polymer with at least an equal quantity of polymerizable monomer, optionally with the aid of a nonpolymerizable penetrating agent, and subjecting the softened mixture to a forming or finishing operation and effecting polymerization in the cold under the influence of electromagnetic or particulate ionizing radiation	310
Brit.	851,647	Fr. Appl. 16.11.57	Rhone Poulenc	Equivalent to Belg. 572,906		See above	311
U. S.	3,107,207	Fr. Appl. 16.11.57	Rhone Poulenc	Equivalent to Belg. 572,906		See above	312

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Fr.	Addition 73,034 Addition to Fr. 1,181,893	18.11.57		Rhone Poulenc	(Process claim)		The grafting process is controlled by mixing the monomer vapor with one or more vaporized substances which increase or decrease the penetration of the monomer into the solid polymer	*CA*, 56, 15684	313
U. S.	3,029,218	25.11.57	10.4.62	Dow	Poly(vinyl lactam) substrate, e.g., poly(*N*-vinyl-pyrrolidinone)	Compound prepared by the reaction of a polyglycol of a specified type with mixtures of monomeric methyl methacrylate and derivatives of organic sulfonic acids such as *p*-toluenesulfonic acid or sodium styrenesulfonate	Claims a composition comprising a graft copolymer of said constituents with poly(acrylonitrile). The addition of said graft copolymer improves the dye-receptivity of the acrylonitrile polymer fibers, decreases the tendering of such fibers to accumulate static electricity charges, and stabilizes the fibers against attack by light, heat, and alkalis	*CA*, 57, 8750	314
U. S.	3,029,219	25.11.57	10.4.62	Dow		Vinyl benzyl polyglycol ethers may be used instead of the dimethacrylate ester of the polyglycol			315
U. S.	3,029,220	25.11.57	10.4.62	Dow		Aminoethylacrylates or methacrylates			316
U. S.	3,035,009	25.11.57	15.5.62	Dow		A mixture of monomers con-			317

						sisting of aminoethyl acrylates or methacrylates and derivatives of organic sulfonic acids that contain a substituent, reactive vinyl or other alkenyl group in its molecule			
U. S.	3,036,032	25.11.57	22.5.62	Dow		Mixtures of monomers of bisacrylamides and organic sulfonic acid compounds			318
U. S.	3,036,033	25.11.57	22.5.62	Dow		Mixtures of monomers of vinylpyridines and organic sulfonic acid compounds			319
Brit.	849,063	U. S. Appl. 25.11.57		Dow	Equivalent to U. S. 3,029,218 3,029,219 3,029,220 3,035,009 3,036,032 3,036,033		See above		320
Brit.	840,153	U. S. Appl. 13.12.57	6.7.60	United States Rubber Co.	Poly(butadiene)	Styrene	Binary blends of a graft polymer made by polymerizing a styrene monomer on poly(butadiene) containing 0–1.0% divinylbenzene with styrene resins exhibit high impact strength	*CA*, 54, 26005	321

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Belg.	573,388	U. S. Appl. 13.12.57		United States Rubber Co.	Equivalent to Brit. 840,153		See above		322
Brit.	894,853	Ital. Appl. 23.12.57	26.4.62	Montecatini	Hydroperoxide of an α-olefin homo- or copolymer, e.g., of poly(propylene) or poly(butene)	Vinyl chloride	Preparing vinyl chloride graft copolymers by polymerizing vinyl chloride in an aqueous medium with a hydroperoxide derivative of an α-olefin homo- or copolymer in the presence of a polyethylene polyamine	*CA*, 57, 3637	323
Austral.	44,407(58)	23.12.57		Montecatini	Equivalent to Brit. 894,853		See above		324
Brit.	899,999	U. S. Appl. 26.12.57		Monsanto	Rubbery butadiene polymer	Styrene	Preparing a styrene-rubber graft polymer by polymerizing styrene in the absence of emulsifying agents other than those employed in the polymerization of the rubbery butadiene polymer. Said rubbery polymer consisting essentially of 50–100 wt % butadiene, 0–50 wt % styrene and up to 1 wt % of a monomer containing a plurality of nonconjugated ethylene groups such that the graft polymer has a composition defined by a triangular graft. The product is intended primarily for preparing blends with rigid styrene polymers		325
Austral.	44,495(58)	26.12.57		Monsanto	Equivalent to Brit. 899,999		See above		326
Ital.	602,489	1.1.58		Montecatini	Poly(propylene)	Mixture of isopropenyl and	Monomer mixture heated (80°C) with poly(propylene) fiber *in vacuo*.	*CA*, 56 1612	327

					methyl methacrylate	Grafting improves receptivity to dyes	
Brit.	910,702	U. S. Appl. 2.1.58 19.12.58	Monsanto	Rubbery polymer of an acrylic aliphatic conjugated diene hydrocarbon	Alkyl acrylate or methacrylate or a mixture with a monovinylidene aromatic hydrocarbon or halohydrocarbon	Claims a mixture of a graft copolymer of said constituents with "hard" polymers. Also claims the production of the graft polymer	328
Austral.	44,692/58	2.1.58 30.12.58	Monsanto	Rubbery polymer of a conjugated 1–3 diene	C_{1-8} alkyl methacrylate and also mixed with a monovinylidene aromatic hydrocarbon	Said monomers are polymerized in the presence of a conjugated 1–3 diene. Grafting is by transfer. Also claims blends of above graft copolymer with a hard vinyl chloride polymer or with a rigid thermoplastic styrene polymer	329
Brit.	872,432 Addition to Brit. 850,471	Ital. Appl. 10.1.58	Montecatini	Linear high mol wt homopolymer of propylene or copolymer of ethylene and propylene	An isopropenylpyridine or in admixture with acrylonitrile styrene or a methacrylate	The affinity to dyes is improved by grafting said monomer(s) onto propylene homo- or copolymers	330
Belg.	574,580	Ital. Appl. 10.1.58	Montecatini	High mol wt linear polymers of α-olefins especially poly(propylene)	Monomers containing at least one isopropenyl group, e.g., 2-isopropenyl pyridine, acrylonitrile styrene, or a methacrylate	The affinity to dyes is improved by grafting said monomer to linear poly(α-olefins).	331
U. S.	3,093,615	Ital. Appl. 10.1.58	Montecatini	Equivalent to Belg. 574,580		See above	332

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Austral.	45,328/59	14.1.58		Dunlop Rubber	A process claim		A process for the production of a graft polymer which comprises subjecting an aqueous dispersion of a polymer and a monomer copolymerizable therewith to ionizing radiation, having an energy greater than 0.1 MeV until the required proportion of monomer has combined with the polymer		333
Brit.	842,841	Fr. Appl. 23.1.58	27.7.60	Societe des Usines Chimiques Rhone-Poulenc	Polydiolefin, e.g., poly(butadiene)	Acrylic or methacrylic ester	A rigid, shock-resistant, thermoplastic composition consists of a mixture of a rigid copolymer of α-methyl styrene and acrylonitrile with a graft copolymer of an acrylic or methacrylic ester onto a polydiolefin	*CA*, 55, 4050	334
Belg.	575,094	U. S. Appl. 27.1.58		American Cyanamid	Cellulose film	Vinyl monomer	At least 0.1 % of the glucose units of a regenerated cellulose film are converted to free radicals and then contacted with the vinyl monomer until at least 15 % has graft copolymerized. The film may be activated by passing it continuously through an aqueous solution of a ceric salt, washing and then passing through an aqueous solution containing at least 1 % of monomer. The film may be impregnated with an initiator of free radicals such as a Co^{3+} salt		335
U. S.	3,038,876	27.1.58	12.6.62	Du Pont	Polyurethanes, polyureas	Acrylic monomers	A solution of an addition polymer, such as an acrylonitrile homopoly-	*CA*, 57, 7474	336

							mer or copolymer with methyl methacrylate in $HCON(CH_3)_2$, dimethyl acetamide, *N*-methylpyrrolidinone or CH_3SO, mixed at 0°C with a solution in the same solvent of bis(4-isocyanatophenyl) methane or tolylene 2,4-diisocyanate plus bis(4-aminocyclohexyl) methane, 2,5-dimethyl piperazine, or $C_2H_4(OH)_2$; reaction occurs at 0° to form a graft comprising addition and condensation polymer segments. Other addition polymers, such as elastomers, may be used as substrates		
U. S.	3,022,264	29.1.58	20.2.62	Dow	Poly(acrylonitrile)	Selected *N*-vinyl lactams, e.g., *N*-vinyl-2-pyrrolidinone	Poly(acrylonitrile) fibers are impregnated with aqueous monomer and irradiated under nitrogen with a 100,000 rep dose from a Van de Graaff generator	*CA*, 57, 1088	337
U. S.	3,022,265	29.1.58	20.2.62	Dow	Poly(acrylonitrile)	Selected aminated alkenyl aromatic compounds, e.g., trimethyl (vinyl benzyl)—ammonium chloride	Poly(acrylonitrile) fibers are impregnated with the aminated compounds and irradiated at room temperature with a Van de Graaff generator	*CA*, 57, 1091	338
U. S.	3,035,010	29.1.58		Dow	Poly(acrylonitrile)	*N*-vinyl-2-oxazolidine monomer	Claims a dye-receptive composition comprising a graft copolymer of said constituents		339
Brit.	881,374	U. S. Appl. 29.1.58	1.11.61	Dow	C_{2-6} nonaromatic monoolefin	Ethylenically unsat. monomers have dye-receptive props. in the polymeric form	Polymer fibers swollen with monomer and irradiated	*CA*, 58 4683	340

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	876,001	29.1.58	1.11.61	Dow	Polyester		Polymer fibers swollen with monomer and irradiated		341
U. S.	3,048,561	29.1.58		Dow	Poly(acrylonitrile)	Vinylpyridine monomer	Claims a dye-receptive composition of an acrylonitrile polymer with vinylpyridine grafted side chains		342
U. S.	3,049,507	29.1.58		Dow	A polyolefin of a 2 to 6 carbon atom nonaromatic hydrocarbon monoolefin	*N*-vinyl lactam monomer	Claims a dye-receptive composition comprising a graft copolymer of said constituents		343
U. S.	3,049,508	29.1.58		Dow	Polyolefin of a 2 to 6 carbon atom, nonaromatic monoolefin	A vinylpyridine monomer, an alkenyl aromatic monomer, or an aminated acrylate or methacrylate monomer or mixtures thereof	Claims a dye-receptive graft copolymer composition comprising said constituents		344
U. S.	3,050,498	29.1.58	21.8.62	Dow	Poly(acrylonitrile)	Dimethylamino ethyl acrylate	Dye-receptive graft copolymer compounds are prepared by impregnating poly(acrylonitrile) aquagel fibres with 6% aqueous dimethyl amino ethyl acrylate for 15 min and irradiated for 25 min at 40,000 rads/hr	*CA*, 57, 14001	345
Brit.	901,042	U. S. Appl. 29.1.58		Dow	Polyamide, e.g., nylon 66	Vinyl lactam, a sulfonated alkenyl aromatic monomer, a sulfonated olefin,	Claims a dye-receptive polyamide formed by grafting said monomer onto the polymer		346

					a sulfonated acrylate, vinylpyridine, aminated alkenyl aromatics, monomers, polyglycol esters of acrylates or methacrylates or *N*-vinyl-3-morpholine		
Brit.	905,465	U. S. Appl. 29.1.58	Dow	Poly(acrylonitrile)	*N*-vinyl lactam, *N*-vinyl-3-morpholinone, sulfated alkenyl aromatic, sulfonated olefin, aminated alkenyl aromatic, aminated ethyl acrylate or methacrylate or alkenyl aromatic polyglycol ether monomers or mixtures thereof	Claims a dye-receptive graft copolymer comprising poly(acrylonitrile) grafted with said monomer	347
Fr.	Addn. 72,867 Addition to Fr. 1,130,099	31.1.58	Centre National de la Recherche Scientifique	Poly(tetrafluoroethylene). poly(trifluorochloroethylene)	Methyl methacrylate, styrene	A modification to the process described in the parent patent for grafting a monomer into the mass of a polymer difficult to graft in depth, whereby the monomer is diluted with a solvent (e.g., benzene) capable of reducing the grafting rate without affecting the rate of diffusion of the said monomer into the polymer	348

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	3,020,257	12.2.58		Haris Co.	Poly(isobutylene)	Vinyl acetate	Vinyl acetate dissolved in a ketone solvent is polymerized in the presence of poly(isobutylene) using a specified "circulation" technique. Product may be used as a substitute for chicle in chewing gum		349
Fr.	Addn. 72,879 Addition to Fr. 1,130,099	12.2.58	29.4.60	Centre National de la Recherche Scientifique	Poly(tetrafluoroethylene)	Styrene	The mixture of polymer and monomer is irradiated (*in vacuo*) so that the monomer is allowed to penetrate in the partially grafted copolymer without copolymerization during the periods between successive irradiations	*CA*, 57, 1090	350
Brit.	901,736 (cf. Australian application 45,328/59; applied 14.1.58)	14.2.58		Dunlop Rubber	Synthetic elastomer, e.g., butadiene-styrene, butadiene-acrylonitrile, butadiene-methylisopropenylketone, poly(propylene), ethylene-propylene copolymer, or poly(butadiene)	Monomers containing one C=C double bond, e.g., vinyl esters, vinylidene compounds, alkyl methacrylates, and acrylates	An aqueous dispersion of a synthetic elastomer and a monomer copolymerizable therewith is subjected to ionizing radiation having an energy greater than 0.1 Mev until the required proportion of the monomer has combined with said synthetic elastomer		351
Brit.	892,189	U. S. Appl. 5.3.58		Monsanto	Poly(methyl acrylate)	Monovinylidene aromatic hydrocarbon, e.g., styrene	An aqueous composition containing methyl acrylate and a polymerization catalyst is slowly added to an aqueous medium of an anionic or nonionic emulsifying agent at a constant rate, followed by the addition of the monovinylidene aromatic hydrocarbon. The graft		352

							interpolymer latex so formed can be used for paper coating		
U. S.	3,099,631	6.3.58	30.7.63	Du Pont	High mol wt., linear, nitrogenous condensation polymer, e.g., a polyamide	Monomeric acid	Claims a graft copolymer substantially insoluble in water from the class consisting of said polymer with grafted acid groups. The acid groups may also be in the form of a salt. A foam of the graft copolymer is also claimed	*CA*, 60, 9410	353
U. S.	3,068,122	10.3.58		Du Pont	Hydrocarbon polymer polyester, polyamide polyether	Ester of an unsaturated alcohol being capable of forming metal chelates	The polymeric substrate is subjected to ionising radiation prior to treatment with a chelated ester		354
Brit.	844,331	12.3.58		Adhesive Tapes Ltd.	Natural rubber	Methyl methacrylate	A natural rubber grafted with poly(methyl methacrylate) is used in place of all or part of the natural rubber in an adhesive composition		355
Brit.	905,043	U. S. Appl. 17.3.58		Du Pont	Cross linkable polymer, e.g., poly(ethylene), copolymer of ethylene with another 1-olefin, or butadiene rubber	Vinyl chloride	Polymer is irradiated in the presence of vinyl chloride vapor to form a crosslinked graft copolymer		356
U. S.	3,046,078	18.3.58		American Cyanamid	Cellulosic material	Vinyl monomer	A graft copolymer is formed by continuously contacting and wetting a cellulosic material with an acidic dispersion of a ceric salt and passing the material through an atmosphere of a polymerizable monomer in the vapor state		357

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
Brit.	916,245	U.S. Appl. 27.3.58 2.6.58		Theodore Alcott Tegrotenhuis	Rubbery polymers and copolymers of diolefinic compounds (including polymers of butadiene, chloroprene, isoprene, dimethyl butadiene, and copolymers of such with styrene or acrylonitrile)	Monoolefin	Claims a graft copolymer of said constituents for use in metal coating compositions	358
U. S.	2,984,608	31.3.58		Nobel-Bozel	Paraffinic hydrocarbon composition of at least one hydrocarbon of the C_nH_{2n+2} containing not more than 20% of unsaturated hydrocarbon as impurities therein	Vinyl monomer	A graft polymer composition is prepared by exposing a gel of said polymer and a vinyl base polymerizable monomer at approximately 50°C to high energy ionizing radiation	359
U. S.	3,090,664	31.3.58		Du Pont	Nitrogen containing polymeric materials	Unsaturated organic acid, e.g., acrylic acid	The shaped polymeric material is exposed to an organic acid followed by irradiation with UV rays. The graft copolymer so formed has improved resistance to static accumulation	360
Brit.	855,720	7.4.58		Dow	Polyolefin, e.g., poly(ethylene) or poly(propylene)	Acrylonitrile	A method of making an oriented graft copolymer structure such as fiber, etc., by treating a polymer of specified dimensions to the action of ozone in an inert fluid medium. The ozonized polymer is then reacted with acrylonitrile,	361

							and orientated by stretching the thus formed grafted structure in at least one of its dimensions by an amount corresponding to at least 10% of the initial dimension		
Brit.	860,327	U. S. Appl. 7.4.58		Midland Silicones	Specified organosiloxane polymer	Ethylene, propylene, vinyl chloride, butadiene, tetrafluoroethylene, trifluorochloroethylene, vinyl dichloride, vinyl carbazole, or isoprene	The polymer is exposed to ionizing radiation at a temperature at least as low as the 2nd order T.T. and in substantial absence of oxygen and then contacted with said monomer. The temperature of the reactants is then raised above the 2nd order T.T. whereupon a grafting reaction occurs		362
Fr.	1,228,366	U. S. Appl. 7.4.58		Dow Corning Corp.	Organopolysiloxanes				363
U. S.	3,008,885	16.4.58	14.11.61	Nobel	Celluloeic material	Vinyl acetate	A mixture of a cellulose compounds with at least one polymerizable monomer is exposed to high energy radiation *in vacuo* and in the presence of hexahydro-1,3,5-triacryloyl-S-triazine (I). If I is omitted, the exposure must be increased in order to achieve similar results	*CA*, 56, 11824	364
U. S.	3,070,574	Ger. Appl. 16.4.58		B.A.S.F.	Poly(α-methylstyrene)	Styrene, butadiene, isoprene, or vinylcarbazole	α-Methyl styrene is polymerized in the presence of an alkali metal (or its hydride) and in the presence of a cyclic ether (THF or dioxane). The selected monomer is then added and the reaction continued to form a linear graft copolymer		365

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	3,065,041	23.4.58		American Cyanamid	Paper	Ethyl acrylate, propyl acrylate, or butyl acrylate	Graft polymerising said monomer, in the presence of ethylene dimethylacrylate, onto a paper substrate in an aqueous medium at a pH not greater than 3.5 and in the presence of a ceric salt which is soluble in at least one component of the reaction medium until the weight of monoacrylate grafted onto the substrate is between 100 and 900%		366
Brit.	901,646	U. S. Appl. 25.4.58	25.7.62	Monsanto	Conjugated 1,3-dienes	Monovinylidene aromatic hydrocarbons, acrylonitrile, and methacrylonitrile	An aqueous dispersion of the diene polymer is dispersed and polymerized with 15–90 parts by weight of a mixture of olefins per 100 parts rubbery polymer	*CA*, 58, 2549	367
Austrl.	48177/59	26.4.58		Monsanto	Equivalent to Brit. 901,646		See above		368
Brit.	845,052	28.4.58		Adhesive Tapes	Natural or synthetic rubber	Methyl methacrylate	A natural rubber grafted with methyl methacrylate and compounded with a butadiene-acrylonitrile copolymer is used in coating formulations for adhesive applications		369
Fr.	1,229,071	Jap. Appl. 28.4.58		Agency of Industrial Science and Technology	Synthetic high polymer	Heterocylic monomer containing three structural groups such as ethylene oxide or ethylene sulfide	A process for improving the dye-affinity of synthetic high polymers by exposing them in their final form to irradiation in the presence of a heterocyclic monomer containing three structural groups; the process may be carried out in two stages, viz., irradiation, then		370

					(Process claim)		heating in the presence of the monomer		
Brit.	871,192	2.5.58		I.C.I.	Water soluble polymers, e.g., poly(vinyl alcohol) poly(ethylene oxide), poly(vinyl) pyridine), poly(acrylic acid), poly(methacrylic acid), the amides of poly(acrylic) and poly(methacrylic) acids, starches, dextrins, starch ethers, and cellulose ethers	Monomeric ethylenically unsaturated compound of specified structure, eg., acrylonitrile or acrylamide	Water soluble grafted polymers are obtained by polymerizing said monomer in the presence of a water soluble preformed polymeric substance		371
U. S.	3,075,857	Ital. Appl. 2.5.58		Montecatini	Poly(propylene)	Acrylonitrile	Patent claims use of a poly(propylene-g-acrylonitrile) copolymer as an intermediate layer in a laminated film wrapper. The secondary layers may be PVC, PVAlc, PVA, or copolymers of vinyl chloride and vinylidene chloride with vinyl acetate of acrylonitrile		372
U. S.	3,087,875	8.5.58	30.4.63	Rohm and Haas	Poly(alkyl methacrylate)	Acrylates, thioacrylates, methacrylates, thiomethacrylates, acrylonitrile, methacrylonitrile, acrylic or methacrylic acids	The polymeric substrate is exposed to ionizing radiation in the absence of oxygen and in the presence of specified monomer	*CA*, 59, 1781	373

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Fr.	1,228,507	U. S. Appl. 8.5.58		Rohm and Haas	Equivalent to U. S. 3,087,875		See above		374
Brit.	916,217	U. S. Appl. 8.5.58		Rohm and Haas	Equivalent to U. S. 3,087,875		See above		375
U. S.	2,996,469	14.5.58		Firestone Tire and Rubber Co.	Homopolymers of vinyl chloride or copolymers thereof with ≤20% other unsaturated compounds	Mixture of a diene, e.g., butadiene, isoprene, 2,3-dimethyl butadiene, or piperylene and a nitrile, e.g., acrylonitrile, methacrylonitrile or α-ethylacrylonitrile	Graft copolymers of said constituents are prepared by a transfer mechanism using $K_2S_2O_8$ as initiator. The products have excellent adhesion to metal. The films have good transparency	*CA*, 56, 3638	376
U. S.	2,996,470	14.5.58	15.8.61	Firestone Tire and Rubber Co.	Poly(vinyl chloride)	Mixture of 1,3-butadiene, acrylonitrile, and an unsaturated carboxylic acid	Claims latexes containing polymer prepared by grafting said monomer mixture in the presence of a mercaptan and without added catalyst, onto a PVC substrate made by emulsion polymerization. Product may be used for coating metals	*CA*, 60, 12234	377
Belg.	577,722	Ger. Appl. 15.5.58		Farbwerke Hoechst	Polyalkylene glycols and/or their derivatives	Vinyl esters, acrylates or methacrylates or mixtures of these monomers	Process for preparing graft polymers of polyvinyl esters, polyacrylates, and polymethacrylates by dissolving polyalkylene glycols and/or their derivatives in said monomer with or without addition of other		378

						solvents and polymerizing the solution obtained with the addition of free radical catalysis and/or irradiation	
Belg.	578,864	22.5.58	Du Pont	Propadiene	Butene-1	Polymers of a specific kind, composed of a normally solid high mol wt polymer of propadiene, and at least one other polymerisable hydrocarbon compound with a terminal ethylenic unsaturation which polymer contains grafted methylene and vinyl groups	379
U. S.	3,067,163	22.5.58	Rohm and Haas	Polymers of long chain alkyl or vinyl esters	Nitrogen containing monomers	A process for preparing oil soluble, dispersing graft copolymers which comprises polymerizing nitrogen containing monomers in the presence of a partially polymerized polymer of a long chain alkyl or vinyl ester	380
Brit.	926,477	U. S. Appl. 26.5.58	American Machine and Foundry Co.	Film forming polymer, e.g., poly(ethylene) or poly(propylene)	Ethylenically unsaturated liquid monomer, e.g., styrene	A process for the production of shaped products such as sheet materials that comprises hot forming a composition that has been produced by exposing a granular polymer swollen with monomer to the action of heat, a free radical catalyst and/or irradiation	381
Brit.	926,478 (divided out of Brit. 926,477)	U. S. Appl. 26.5.58	American Machine and Foundry Co.	Water insoluble film-forming polymer other than a polyalkylene	Liquid ethylenically unsaturated monomer	Ion exchange material is prepared by swelling a water insoluble polymer with said monomer and polymerizing, the monomer having or being provided with ion exchange groups or chelation groups	382

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
U. S.	3,014,008	2.6.58		Eastman Kodak	Copolymer of a vinylpyridine and acrylonitrile, a vinyl ester of a saturated monobasic fatty acid, an *N*-alkyl acrylamide, or an *N*,*N*-dialkylacrylamide	Monomer mixture consisting of acrylonitrile, a vinyl ester of a saturated monobasic fatty acid, an unsubstituted vinyl pyridine, an alkyl substituted vinyl pyridine, and an alkyl acrylate	Claims a graft copolymer of said constituents polymerized in specified proportions	383
Brit.	844,141	U. S. Appl. 8.6.58		United States Rubber Co.	Poly(butadiene)	Styrene acrylonitrile mixture	Claims a high impact injection moldable material containing at least 5% of a graft copolymer of said constituents prepared by transfer during latex polymerization	384
Brit.	903,715	12.6.58		B. X. Plastics	Vinyl chloride polymer or copolymer and an elastomer, e.g., polymerized vinyl caprate, vinyl caprylate, or vinyl laurate	Vinyl ester of a fatty acid	A process for the manufacture of PVC compositions yielding rigid clear products, wherein a vinyl chloride polymer is compounded at a temperature of at least 50° with an organic compound that is polymerizable to an elastomer and the compounded material is subjected to ionizing radiation to polymerize this organic compound, so that the vinyl chloride polymer and the elastomer are present in the resultant product in intimate admixture	385

Ger. (D.A.S.)	1,081,230	3.7.58		Farbwerke Hoechst	*N*-containing poly-alkylene glycols and/or oxides and/or their derivatives	Vinyl esters	Said polymers are dissolved in vinyl esters with or without other solvents and the mixture is polymerized with a free radical activator or by irradiation		386
U. S.	3,029,221	17.7.58	10.4.62	Union Carbide	Poly(styrene)	Methyl methacrylate	α-β compounds are first polymerized in an anhydrous medium to soluble polymers. Alkali metal hydrocarbons polymerize the monomer without chain termination or chain transfer reactions. Compounds containing active H may be treated with above soluble polymers to form a graft polymer of controlled mol wt	*CA*, 57, 16893	387
U. S.	2,979,447	18.7.58		Dow	Fibre forming acrylonitrile polymer aquagel	Specified *N*-vinyl-cyclic amide or *N*-vinylcyclic carbamate or mixtures thereof	The dyeability of acrylonitrile polymers is improved by exposing the aquagel polymer impregnated with said monomer, to the action of ionizing radiation and then within 120 sec after the termination of the exposure subjecting the polymer to a temperature between 90 and 120° for a period between 180 and 20 sec, without irreversibly drying said aquagel, whereby a graft copolymer is formed		388
Fr.	Addn. 73,864 Addition to Fr. 1,222,417	22.7.58		Ethylene Plastique	Poly(ethylene) (Process claim)	Vinyl monomer	A process for grafting a vinyl monomer onto inhibitor-free poly-(ethylene) which is subjected, prior to grafting ,to a sensitizing treatment with heat and/or an ionizing irradiation, preferably in the presence of oxygen or an oxygen-containing gas. Irradiation and thermal treatment may be simultaneous, successive or alternating		389

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Belg.	575,430	Fr. Appl. 22.7.58		Ethylene Plastique	Equivalent to Fr. 73,864		See above		390
Brit.	890,145	Fr. Appl. 22.7.58	28.2.62	Ethylene Plastique	Equivalent to Fr. 73,864		See above	*CA*, 58, 677	391
U. S.	2,990,393	24.7.58		Eastman Kodak	Homopolymer of an unsaturated vinyl pyridine, homopolymer of a vinyl pyridine having a methyl group substituted on the pyridyl nucleus or copolymer of said vinyl pyridine and acrylonitrile	Acrylonitrile	A process for preparing a resinous fiber-forming graft copolymer which comprises heating a mixture of water, a polymerization catalyst, said polymer (having been formed in and not separated from said mixture) and acrylonitrile		392
U. S.	3,097,185	29.7.58		Dow	Poly(vinyl lactams)	Specified acrylamide and methacrylamide monomers	Claims a graft copolymer of certain acrylamide and methacrylamide monomers or polyvinyl lactams and improved acrylonitrile polymer compositions obtainable therewith		393
U. S.	3,010,936	7.8.58		Borg-Warner	Synthetic aliphatic conjugated diolefine hydrocarbon polymer, e.g., poly(butadiene)	Styrene, α-methyl styrene, a vinyl toluene, or α-methyl vinyl toluene	Patent refers to a mechanical blend of a graft copolymer of poly(butadiene) with said constituent and an interpolymer of acrylonitrile, α-methyl styrene and styrene	*CA*, 56, 3660	394
Brit.	892,133	8.8.58	21.3.62	B. X. Plastics	Low gel synthetic rubber, e.g.,	Vinyl, divinyl, or vinylidene	The rubber is swollen with monomer a free radical catalyst added and	*CA*, 57, 2438	395

					butadiene-*co*-styrene	monomers	the mixture heated under specified conditions		
U. S.	3,070,573	18.8.58		Dow Corning Corp.	Organo-silicon compounds	Organic vinylic compounds	A specified organosilicon compound is contacted with ozone at a temperature not greater than 30°C and then contacted above 30°C with an olefinic compound having a terminal group $CX_2{=}C<$ in which X is a specified substituent		396
Brit.	869,482	U. S. Appl. 18.8.58		Midland Silicones	Equivalent to U. S. 3,070,573		See above		397
Brit.	891,944	U. S. Appl. 19.8.58 31.7.59		Du Pont	Linear poly(ethylene)	Acrylic or methacrylic acid or their salts	Claims a plexifilament of a grafted polymer of poly(ethylene) and said monomer. Also claims a process for producing a plexifilament as claimed by subjecting a plexifilament formed from a synthetic organic fiberforming polymer to ionizing radiation while it is in intimate contact with an organic compound as defined		398
Fr.	Addn. 74,130 Addition to Fr. 1,130,100	28.8.58	3.3.61	Centre National de la Recherche Scientifique	Poly(styrene)	Methyl methacrylate, or acrylonitrile	The degradation of the initial polymer is decreased during the irradiation of the reaction mixture by the addition of an oxidation preventing agent such as an alcohol, phenol, or amine. A solvent providing free radicals (such as $CHCl_3$, CH_2Cl or CCl_4) under the action of γ-radiation is also used	*CA*, 56, 15685	399

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Fr.	1,210,101	30.8.58		Nobel-Bozel	(Process claim)		The polymer is first swollen in a monomer capable of graft copolymerizing therewith and then immersed in a second liquid which is a solvent for neither the polymer nor the monomer. The mixture is then subjected to the action of ionizing radiation. The polymer may be in the form of a powder and the immersion liquid (e.g., water) may be used as a carrier for the polymer		400
Belg	581,798	30.8.58		Nobel-Bozel	Equivalent to Fr. 1,210,101		See above		401
Brit.	899,683	Fr. Appl. 30.8.58		Nobel-Bozel	Equivalent to Fr. 1,210,101		See above		402
Fr.	1,211,629	3.9.58		Regie Nationale des Usines Renault	Cellulose	Unsaturated monomers especially styrene	Claims fibrous products based on cellulose, characterized by the fact that unsaturated monomers are grafted onto allylcellulose molecules by polymerizing in bulk, in solution or in suspension in the presence of allylcellulose under specified conditions		403
Brit.	912,280	Fr. Appl. 3.9.58		Regie Nationale des Usines Renault	Equivalent to Fr. 1,211,629		See above		404
Brit.	934,038	4.9.58	14.8.63	Rohm and Haas	Hydrocarbon-soluble polymer	Esters of acrylic or methacrylic acid	Claims the use of a graft copolymer of said constituents for use as a hydrophobic dispersing agent for	*CA*, 60, 5751	405

						polymer dispersions in organic liquid media	
Brit.	917,498	U. S. Appl. 8.9.58 15.9.58	Dow	Elastomeric ethylene substrate being a copolymer of ethylene and at least one other aliphatic olefin	Alkenyl aromatic monomer or an acrylic monomer	Claims a polymer composition consisting of or containing a graft copolymer of said constituents. A process for the preparation of such grafts is also claimed. The polymers are said to possess high elongation, high impact strength and exceptional stability	406
Brit.	917,499 Divided out of 917,498	U. S. Appl. 8.9.58 15.9.58	Dow	Elastomeric ethylene copolymer substrate containing one or more vinyl ester or vinyl ether monomers interpolymerized with ethylene	Alkenyl aromatic monomer or an acrylic monomer particularly acrylonitrile	Claims a polymer composition consisting of or containing a graft copolymer of said constituents. A process for the preparation of such grafts is also claimed	407
Austral.	52,516(59)	U. S. Appl. 8.9.58 15.9.58	Dow	Equivalent to Brit. 917,498–9		See above	408
Brit.	897,705	U. S. Appl. 24.9.58	Borg Warner Corp.	Conjugated polydiolefin, e.g., poly(butadiene)	Vinyl aromatic hydrocarbon or an alkyl-substituted vinyl aromatic hydrocarbon, vinyl cyanide or an alkyl-substituted vinyl cyanide	Claims a blend of a graft copolymer of said constituents and a polyurethane rubber	409
Austral.	52,520(59)	Brit. Appl. 16.9.58	Smith and Nephew	Natural rubber	Alkyl methacrylate	Claims a pressure-sensitive adhesive sheet material containing a graft copolymer of natural rubber and an alkyl methacrylate	410

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Belg.	571,542	26.9.58	26.3.59	Solvic	Poly(vinyl chloride)	Unsaturated monomers e.g., styrene, acrylic or methacrylic acid, acrylonitrile, vinyl acetate or chloride, vinylidene chloride, or 1,3-butadiene	Dehydrochlorination of PVC is followed by oxidation (O$_2$ or peroxide) yielding a polymer containing an easily controlled number of activated groups. The peroxidized polymer is then copolymerized with one or more unsaturated compounds	*CA*, 53, 16599	411
Germ. (D.A.S)	1,083,051	4.10.58		Deutshe Gold und Silber-Scheideanstalt	Polymers or copolymers of acrolein or α-substituted acrolein	Macromolecular compounds	Polymers or copolymers of acrolein or α-substituted acrolein are reacted with macromolecular compounds having per mol not less than 4 groups capable of reacting with aldehyde groups		412
Belg.	583,429	Germ. Appl. 10.10.58		B.A.S.F.	Polymer containing reactive groups (Process claim)	Unsaturated monomer	A process for preparing graft copolymers by grafting a monomer onto a polymer with reactive groups in the chain, characterised in that the starting polymer is treated with halogens, hydrogen halides, halogen oxyacids, or their salts, or with halogen oxides and then treated with an unsaturated polymerizable monomer		413
U. S.	3.092,512	13.10.58		Du Pont	Synthetic linear polyamide, polyurethane, polyurea, or polysulfonamide	Hydrocarbon monomers. Each grafted side chain is attached by a single C-C bond to a catenarian carbon of the linear polymer	A graft copolymer composition comprising a product prepared by polymerizing an alkenyl substituted aromatic compound in the presence of a preformed copolymer of an alkenyl substituted aromatic compound and a conjugated diene		414

Brit.	858,747	U. S. Appl. 29.10.59		Shell Internationale Research Maatschappij	Copolymer of an alkenyl substituted aromatic compound and a conjugated diene containing 5–7 carbon atoms, e.g., styrene-isoprene or 2,3-dimethyl buta-1,3-diene	Alkenyl substituted aromatic compound, e.g., styrene	Claims a graft copolymer composition comprising a product prepared by polymerizing an alkenyl substituted aromatic compound and a conjugated diene		415
Austral.	53,999(59)	U. S. Appl. 29.10.58		Shell Internationale Research Maatschappij	Equivalent to Brit. 858,747		See above		416
Brit.	863,395	29.10.58	22.3.61	Distillers	Poly(ethylene)	Vinyl chloride	Poly(ethylene) is irradiated under nitrogen in the presence of benzene and vinyl chloride. The product has a superior stress cracking resistance than a sample treated similarly but in the absence of vinyl chloride	*CA*, 55, 17094	417
Belg.	578,271	U. S. Appl. 31.10.58 31.12.58		Du Pont	Fiber forming polymer	Specified monomer	Graft copolymer of a fiber forming polymer having grafted lateral polymer chains said lateral chains in nongrafted form being soluble in a liquid or swelling to a substantial amount in said liquid, which liquid is a nonsolvent for the graft copolymer, with the characteristic that the article has a definite shape, which is preserved or which reappears when the article is wetted by said liquid		418

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	2,987,501	5.11.58		Dow	Poly(ethylene) or poly(propylene)	Acrylonitrile, lower alkyl esters of methacrylic acid or lower alkyl esters of acrylic acid which esters contain from 1–4 C atoms in the alkyl group	Poly(ethylene) or poly(propylene) is reacted with NO_2, N_2O_4 or mixtures thereof, at between 20 and 100°C whereby reactive sites are produced in the polymer molecule. The so treated polymer is then reacted with said monomer at between 50° and the boiling point of the monomer		419
Brit.	876,535	U. S. Appl. 5.11.58 29.10.59		Dow	Poly(ethylene), poly(propylene), or ethylenepropylene copolymers	Acrylic acid	The polymer is exposed in the presence of air or oxygen to either a radiation dose of 0.5–10 Mr or to 1–10% by vol ozone. The initial grafting is then performed with the polymer in an undissolved state so as to avoid destroying the active polymerization sites. Grafting is done at 65–175° in the substantial absence of air with the polymer slurried in a saturated hydrocarbon containing the acrylic acid	*CA*, **56**, 7517	420
Austrl.	54,115/59	U. S. Appl. 5.11.58		Dow	Polymerised monoolefin containing 2–3 C atoms in the molecule	Monoethylenically unsaturated carboxylic acid especially of acrylic acid and/or methacrylic acid	Claims a graft copolymer of said constituents 98–75% of polymerized monomer and 2–25% of preformed polymer		421
U. S.	2,989,420	13.11.58		Rohm and Haas	Copolymer of butadiene and styrene	Methyl methacrylate and iso-	A felt base type of floorcovering material having a decorative coat-		422

						bornyl methacrylate	ing over which there is a coating comprising a graft copolymer of a mixture of said methacrylates, and a butadiene-styrene copolymer		
Brit.	935,996	14.11.58	4.9.63	B. X. Plastics	Butadiene-acrylonitrile copolymer	Styrene or mixtures with acrylonitrile or methyl methacrylate	The monomer mixture is polymerized in the presence of a butadiene-acrylonitrile latex using $K_2S_2O_8$ to initiate the graft copolymerization	*CA*, 59, 12998	423
Brit.	872,532	Ger. Appl. 29.11.58		Rohm and Haas	Polymer containing hetero atoms, e.g., polymer or copolymer of an ester, amide nitrile or anhydride of acrylic, methacrylic crotonic, maleic, fuonaric, or itaconic acid	Ethylenically unsaturated monomer, e.g., styrene, α-methylstyrene, vinyl naphthalene, isoprene, butadiene, olefins, esters, nitriles, amides of acrylic or methacrylic acid, etc.	A process for the production of graft polymers in which said monomer is polymerized in the presence of an anionic catalyst. Said polymer is added either initially or after the beginning of the process but before the polymerization of the monomer has been completed		424
Belg.	585,104	Ger. Appl. 29.11.58		Rohm and Haas	Equivalent to Brit. 872,532		See above		425
Ger. (D.A.S.)	1,080,304	13.12.58		Farbwerke-Hoechst	Polyalkylene glycols	Vinyl esters	Vinyl esters are polymerized onto polyalkylene glycols or their derivatives in aqueous medium in the presence of known activates and emulsifiers with intensive stirring to form graft copolymers in bead form		426

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
Ger. (D.A.S.)	1,084,917	17.12.58		Farbwerke-Hoechst	Polyalkylene oxides and/or polyalkylene glycols and/or polyalkylene glycol derivatives	Acrylic acid esters	Graft polymerization of said polymers with acrylic acid esters or their derivatives as in Ger. 1,077,430 is carried out by solution in further solvent with addition of radical activators and/or irradiation in known manner	427
U. S.	3,111,501	19.12.58		United States Rubber Co.	Poly(butadiene)	Styrene and acrylonitrile	Claims a gum-plastic comprising α-methyl styrene, acrylonitrile resin and a graft copolymer of styrene and acrylonitrile or poly(butadiene). The material containing specified proportions of the components, has good properties at high temperatures and is very resistant to loss of liquid through pores when used for piping which is subject to fluid pressure	428
Brit.	861,948	U. S. Appl. 23.12.58		Du Pont	Poly(2,3–dichloro-buta–1,3–diene)	Chloroprene	An elastomeric graft copolymer from 8 to 70% by wt of units derived from 2,3-dichlorobuta-1,3-diene the remaining units derived preponderately from chloroprene, the polymer being less than 50% soluble in boiling benzene and having, when cured, a brittle point below −30°C. The preparation of the graft using a free radical catalyst is also claimed	429
Brit.	872,515	U. S. Appl. 30.12.58		Du Pont	Synthetic linear condensation polyamide, e.g., poly	Vinyl monomer of specified formula, e.g., styrene,	Process for the preparation of a graft copolymer in which a polyamide is contacted with said monomer in the	430

					(hexamethylene adipamide) or poly(caproamide)	2,5-dichlorostyrene, vinylidene chloride, methacrylamide, methyl acrylate, ethyl acrylate, vinyl acrylate, acrylonitrile, etc.	absence of any polymerization catalyst and at a temperature of at least 25°C but below the melting point of the polyamide		
Fr.	1,241,563	U. S. Appl. 30.12.58		Du Pont	Equivalent to Brit. 872,515		See above		431
Brit.	946,071	1.1.59		B. X. Plastics			A composition comprising a blend of (1) a crosslinked graft synthetic rubber product obtained by the process described in Specification 935,996, and (2) a resin selected from copolymers (including graft and series polymers) of a styrene and any one or more other monomers, e.g. a styrene-acrylonitrile copolymer		432
Japan	3,300(62)	6.1.59	1.6.62	Japan Radiation High Polymer Research Association	Cellulose	Styrene, methyl methacrylate, vinyl acetate	Cellulose is saturated with water, immersed in the monomer together with a free radical initiator and heated	*CA*, 58, 11544	433
U. S.	3,026,202	7.1.59		Dow	Linear polymeric carbonamide	*N*-vinyl-3-morpholinone	Patent refers to a dye-receptive graft copolymer composition, containing *N*-vinyl-3-morpholinone grafted polyamide		434

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	3,058,950	7.1.59	16.10.62	Dow	Polyolefins	*N*-vinyl-3-morpholinone	Polymer fiber immersed in monomer, excess removed by squeezing and then exposed to x-radiation. Graft copolymer formed has improved dye-receptivity	*CA*, 58, 3543	435
U. S.	3,090,766	7.1.59		Dow	Synthetic linear polyester (which is a condensation product of glycol, and a dicarboxylic organic acid and contains recurring ester groups as an integral part of the main polymer chain)	*N*-vinyl-3-morpholinone	Patent refers to a dye-receptive composition consisting of a graft copolymer of a linear polyester and *N*-vinyl-3-morpholinone		436
U. S.	3,133,041	7.1.59	12.5.64	Dow	Poly(acrylonitrile)	*N*-vinyl-3-morpholinone	Improved dye receptivity is obtained when poly(acrylonitrile) is spun into a $ZnCl_2$ coagulating bath, the aquagel fiber washed, impregnated with *N*-vinyl-3-morpholinone by passing through a solution of the monomer under nitrogen irradiated under nitrogen, dried and dyed	*CA*, 61, 1999	437
Fr.	1,241,564	U. S. Appl. 9.1.59		Du Pont	Condensation polymer	Vinyl monomers	Process for the preparation of a grafted linear condensation polymer, in which the molten polycondensate is contacted with a molten modifying agent of formula $Cx_2=Cx_2$ where x is H, an organic radical or an inorganic radical, with the proviso that at least one of the x atoms is not H		438

U. S.	3,088,791	6.2.59	Du Pont	Synthetic fibers, poly(ethylene)	Styrene sulfonate, acrylates, vinyl acetate	The shaped polymer substrate is exposed to ionizing radiation at a temperature less than 10°C, then contacted with monomer and heated between 25 and 100°C		439
Japan	8,340(61)	6.2.59	Compounds Research Association	Poly(vinyl alcohol)	Water insoluble monomers	Poly(vinyl alcohol) fiber or film is swollen with water, contacted with a water insoluble or very slightly water soluble monomer and polymerized under the influence of catalyst and heat		440
Japan	9,992(61)	6.2.59	Japan Radioactive and High Molecular Research Institute	Poly(vinyl alcohol)	Styrene, alkyl methacrylates	Poly(vinyl alcohol) is soaked in an aqueous solution containing the monomer and then irradiated with ionizing radiation in the presence of air; or it is first irradiated and then soaked to give graft copolymers	*CA*, **56** 6187	441
Fr.	1,247,235	U. S. Appl. 6.2.59	Eastman Kodak	Poly(styrene)	α-olefins, e.g., ethylene or propylene	Styrene is polymerized in the presence of a catalytic mixture containing a trialkylaluminium and a vanadium halide, to form a solid styrene polymer, and an α-olefin such as ethylene or propylene is polymerized in the presence of the poly(styrene) to form a solid graft copolymer		442
U. S.	3,118,854	25.2.59	Goodyear Tire and Rubber Co.	Rubbery polymer of a vinyl aromatic monomer, a conjugated diene monomer and acrylonitrile	Acrylonitrile or styrene-acrylonitrile mixture	Acrylonitrile is polymerized in the presence of said polymer to give transfer grafting. The graft polymer as claimed may be blended with PVC, butadiene-styrene copolymers, poly(styrene) or polyacrylate esters		443

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Austral.	57,527(60)	U. S. Appl. 25.2.59		Goodyear Tire and Rubber Co.	Equivalent to U. S. 3,118,854		See above		444
Brit.	866,667	U. S. Appl. 25.2.59		Goodyear Tire and Rubber Co.	Equivalent to U. S. 3,118,854		See above		445
U. S.	3,083,172	26.2.59	26.3.63	Rohm and Haas	Poly(vinyl acetate)	Acrylic esters	Aqueous emulsion coating compositions having equal durability but superior flow leveling characteristics to acrylic ester polymers are obtained by grafting one or more such esters to a preformed vinyl acetate polymer in the presence of an incompletely saponified poly(vinyl acetate)	*CA*, 59, 1810	446
Brit.	941,064	U. S. Appl. 26.2.59		Rohm and Haas	Equivalent to U. S. 3,083,172		See above		447
Austrl.	57,465/60	U. S. Appl. 26.2.59		Rohm and Haas	Equivalent to U. S. 3,083,172		See above		448
Fr.	1,226,657	26.2.59		Societe des Usines Chimiques Rhone-	Cellulose acetate	Vinyl monomers	Shaped cellulose acetate articles are impregnated with a solution of a polymerization initiator in a liquid having a swelling effect on the		449

				Poulenc			polymer and exposed while heating to vapors of polymerizable monomers, preferably diluted with the vapors of nonreactive liquids		
Brit.	865,263	Fr. Appl. 26.2.59		Rhone-Poulenc	Equivalent to Fr. 1,226,657		See above		450
Ger.	1,111,390	4.3.59		B.A.S.F.	Rubbery copolymers	Styrene or its derivatives	Anionic graft polymerization of styrene is carried out by polymerising styrene or styrene derivatives onto rubbery copolymers of olefinically unsaturated hydrocarbons containing organolithium compounds as structural units in the polymer chain in such a manner that a graft polymer is obtained containing 5–40% rubbery copolymers		451
U. S.	3,044,972	11.3.59	17.7.62	American Cyanamid	Poly(vinyl alcohol) or a polysaccharide such as hydroxyethyl cellulose, starch or amylose	Ethyl or butyl acrylate with or without acrylonitrile	Claims a blend of increased impact strength comprising poly(styrene) and a graft copolymer of said constituents	*CA*, 57, 11401	452
Brit.	869,501	U. S. Appl. 13.3.59		A. E. Staley Manufacturing Co.	Starch	Acrylic monomers, styrene or vinyl acetate	Chemically modified starch is prepared by reacting a granular nonpasty amylaceous product with a vinyl monomer in the presence of an oxidising agent, to produce a graft coploymer		453

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	894,753	U. S. Appl. 23.3.59		C. N. R. S. and Dow	Poly(ethylene)	Acrylonitrile and/or vinylpyrrolidone	Poly(ethylene) is first irradiated to a specified dose in the absence of oxygen whereby active centers are formed on the polymer molecule, then contacting within 5 min of irradiation at least a portion of the so formed active centers on the poly(ethylene) with oxygen and thereafter contacting the oxygenated polymer with a monomer capable of being polymerized by free radicals, to form an addition polymer		454
Brit.	946,404	U. S. Appl. 1.4.59	15.1.64	Shawinigan Resins Corp.	Ethyl cellulose	Vinyl esters especially vinyl acetate	Graft copolymer prepared by polymerising a specified mixture of vinyl ester/ethyl cellulose in the presence of a free radical initiator	*CA*, 60, 10825	455
Brit.	924,873	15.4.59		B. X. Plastics	Diene synthetic rubber	Styrene-methyl methacrylate	Clear moldable composition of rubbery polymers are obtained by polymerizing a mixture of styrene and methyl methacrylate in the presence of a diene rubber, which rubber constitutes at least 5% by weight of the final product, and subjecting the product so obtained to a hot rolling or mastication treatment		456
Brit.	950,315	U. S. Appl. 15.4.59		Standard Oil	Polymer prepared by reacting divinyl benzene with iso-	Ethylenically unsaturated monomer, preferably	Said monomer is polymerized in said polymer with a free radical initiator to produce a graft copolymer		457

				butylene at −30°C in the presence of a Friedel-Crafts catalyst	a *N*-containing substituent, e.g., dimethylamino ethyl methacrylate	suitable for use as "an oil soluble viscosity-index-improving multi-functional lubricant addition agent"	
Germ.	1,084,408	16.4.59	Farbenfabriken Bayer	Natural rubber	Methyl methacrylate	Patent refers to the glueing of elastomers to other articles. Graft copolymers of natural rubber with acrylics, particularly methyl methacrylate, are used	458
Fr.	1,231,875	17.4.59	Dow	Rubbery polymers	Vinyl aromatic monomer	Patent refers to a composition comprising a graft copolymer formed by polymerizing a liquid vinyl aromatic monomer onto pulverised "coated" rubber particles	459
Austrl.	59,580/60	U. S. Appl. 24.4.59	Monsanto	Rubbery acrylic-ester polymer	Styrene acrylonitrile	Graft copolymer is prepared by polymerizing a styrene acrylonitrile mixture in an aqueous dispersion containing a rubbery acrylic ester polymer	460
Austrl.	59,581/60	U. S. Appl. 24.4.59	Monsanto	Rubbery acrylic ester polymer	Styrene-alkyl methacrylate	As above, with styrene alkyl methacrylate as monomer mixture	461
Austrl.	59,582/60	U. S. Appl. 24.4.59	Monsanto	Rubbery acrylic ester copolymer consisting of 80–100% by wt of an alkyl acrylate (C_{2-8}) and 20–0% by wt of a vinylidene monomer	Alkyl methacrylate	An alkyl methacrylate is polymerized in the presence of a rubbery acrylic ester copolymer	462

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
Brit.	926,142	U. S. Appl. 24.4.59		Monsanto	Rubbery acrylic ester polymer derived from polymerizing an alkyl acrylate and a vinylidene monomer in the presence of a crosslinking monomer or monomers	Styrene, a nuclear alkylate styrene or a mixture thereof	A graft copolymer of styrene or its derivatives with said polymer is claimed. The patent also covers a blend of the above grafted polymer with a rigid styrene polymer	463
Brit.	927,821	U. S. Appl. 24.4.59		Monsanto	Rubbery acrylic ester polymer derived from polymerizing an alkyl acrylate and a vinylidene monomer in the presence of a crosslinking monomer or monomers	Styrene or its derivatives and acrylonitrile or an alkyl methacrylate or an alkyl methacrylate and acrylonitrile or a vinylidene monomer other than acrylonitrile	A graft copolymer of said constituents is claimed together with a blend of above grafted polymer and a specified rigid styrene interpolymer	464
Brit.	940,200	U. S. Appl. 24.4.59		Shawinigan Resins Corp.	Polyoxyalkylene (block copolymer of ethylene oxide and propylene oxide)	Vinyl ester	An aqueous emulsion of the components is initiated with a free radical catalyst. The emulsions are useful for heat-seal coatings	465
U. S.	3,028,359	27.4.59		Inter-chemical Corp.	Ethoxyline resin	(a) 3–27% by wt of a nonalkylic alcohol containing the norbornene nucleus (b) 38–82% of an acrylic ester	Patent covers addition polymerisation products of said monomers onto a ethoxyline resin. Grafting is by transfer	466

						(c) 0–32% of at least one monomer selected from methacrylic acid α-vinyl toluene			
U. S.	3,074,906	27.4.59	22.1.63	Borg-Warner Corp.	(A) Conjugated aliphatic diolefin homopolymer or conjugated aliphatic diolefin-monovinyl aromatic hydrocarbon polymer (B) Conjugated aliphatic diolefin monovinyl aromatic hydrocarbon copolymer	(A) Mixture of styrene, α-methyl styrene, vinyl toluene or α-methyl toluene with acrylonitrile or methacrylonitrile (B) Alkyl alkacrylate or a mixture of an alkyl alkacrylate and monovinyl aromatic hydrocarbon	Patent refers to a blend comprising the graft copolymers obtained from polymerization of said constituents in A and B	*CA*, 58, 14248	467
Brit.	937,747	28.4.59		B. X. Plastics	Rubbery copolymer, e.g., of butadiene	Styrene, α-methyl styrene, a vinyl toluene, a chlorostyrene, methyl methacrylate, an acrylate ester, vinylidene chloride, acrylonitrile or an alkyl acrylonitrile or a mixture of any two or more such monomers	Said monomer(s) are grafted onto the rubber copolymer or terpolymer by a transfer reaction. The main claim is to a blend comprising above grafted polymer and a vinyl halide homopolymer or copolymer		468

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
U. S.	3,119,785	5.5.59		General Tire and Rubber Co.	Diene copolymer, or a vinyl chloride polymer or copolymer (polymer must be free of reactive hydroxyl groups)	α-substituted acrolein	An α-alkylacrolein monomer is polymerised with a free radical initiator in the presence of an aqueous dispersion of said organic polymeric material	469
Brit.	946,663	U. S. Appl.		General Tire and Rubber	Equivalent to U. S. 3,119,785		See above	470
Brit.	895,478	Swiss. Appl. 8.5.59		Heberlein	Cellulosic textile material	(i) Substances which are incapable of polymerising such as dyes, organometallic compounds (ii) Substances which have already been polymerized, e.g., PE, PVC, polymethacrylates (iii) Polymerizable substances, e.g., acrylates, styrene, vinyl monomers, etc.	Cellulose is subjected to suitable ionizing radiation at a low dose to form active groups wherein the material is rendered capable of undergoing a graft reaction with a graftable chemical substance. The activated cellulosic textile material is also claimed	471
Austral.	59,120/60	Swiss. Appl. 8.5.59		Heberlein	Equivalent to Brit. 895,478		See above	472
Brit.	922,461	13.5.59		B. X. Plastics	Rubbery interpolymer of butadiene	Styrene or a styrene deriva-	Patent refers to a blend comprising a thermoplastic rigid synthetic	473

					and acrylonitrile	tive ethyl acrylate, vinyl acetate, diallyl phthalate, vinylidene chloride or divinyl benzene, or a mixture of two such monomers	resin with a graft synthetic rubber. The synthetic resin may be a copolymer of styrene and acrylonitrile or of vinyl toluene and acrylonitrile		
Fr.	1,235,424	26.5.59		Societe des Usines Chimiques Rhone-Poulenc	Poly(vinyl alcohol)	Ethylenically unsaturated monomer	Shaped article of poly(vinyl alochol) is impregnated with an aqueous or partly aqueous solution of a radical forming catalyst and then subjected, under radical forming conditions, to the action of an ethylenically unsaturated monomer in the liquid or vapor state		474
Brit.	872,132	Fr. Appl. 26.5.59		Rhone-Poulenc	Equivalent to Fr. 1,235,424		See above		475
Ger.	1,134,834	27.5.59	16.8.62	Licentia Patent-Verwaltungs	Poly(dimethylsiloxane)-poly(methyl methacrylate)		Highly viscous poly(dimethylsiloxane) is mixed with 10% PMMA and 0.2% Bz_2O_2. By heating at 80–100° a graft copolymer with improved properties is obtained when mixed with 25% fine SiO_2 and 1.5% Bz_2O_2 and cured at 120–40°	*CA*, 57, 15372	476
Brit.	935,013	27.5.59	21.8.63	B. X. Plastics	Polyolefin, e.g., poly(ethylene)	Styrene	Poly(ethylene) film is irradiated in the presence of benzophenone, with UV rays, allowed to age in air, and then contact with styrene and a polyalkylene polyamine (in the absence of air) at a temperature that causes swelling but not solution of the film	*CA*, 59, 12990	477

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	3,079,295	29.5.59	26.2.63	Esso Research and Engineering	Conjugated diolefin, e.g., a homopolymer of butadiene or a copolymer of butadiene and styrene	Ethylenically unsaturated crosslinking agent, e.g., vinyl toluene styrene, acrylonitrile, etc.	A resinifiable mix consisting of completely polymerized liquid C_{4-6} conjugated diolefin, a volatile agent for crosslinking the polymer, and a peroxide catalyst is grafted by heating at 200–300°F for 15–320 min. Also claims glass fiber laminates containing said graft copolymer	*CA*, 58, 14255	478
Ger.	1,111,831	U. S. Appl. 29.5.59 19.5.60		Esso Research and Engineering	Equivalent to U. S. 3,079,295		See above	*CA*, 56, 4969	479
Brit.	887,425	U. S. Appl. 29.5.59		Esso Research and Engineering	Equivalent to U. S. 3,079,295		See above		480
Austral.	59,898/60	U. S. Appl. 29.5.59		Esso Research and Engineering	Equivalent to U. S. 3,079,295		See above		481
U. S.	3,100,757	3.6.59		W. H. Smyers, and D. W. Young	Copolymers of styrene and isobutylene	Vinyl chloride	A copolymer of styrene and isobutylene is dissolved in a heat polymerizable monomer consisting mainly of vinyl chloride and the resultant mixture is heated in the presence of a catalyst		482

Brit.	874,067	U. S. Appl. 4.6.59 Brit. Appl. 25.5.60		W. R. Grace	Poly(ethylene)	Styrene	A mixture of poly(ethylene) (I) styrene monomer (II), and a peroxide is homogenized in the absence of a liquid medium at a temperature at least as high as the softening point of the I-II mixture. The unreacted II and styrene homopolymer are extracted from the product	*CA*, 56, 2589	483
USSR	127,392	5.6.59		M. S. Ahutin et al.	Synthetic and natural polymers, e.g., poly(tetrafluoroethylene)	Methyl methacrylate or ethyl acrylate	The polymer molecule is broken up into free macroradicals by means of an electrohydraulic effect, produced by an impulse high voltage electrical discharge. The macroradicals initiate graft copolymerization of the added monomer		484
U. S.	3,030,326	10.6.59	17.4.64	National Starch and Chemical Corp.	Polyethers	Vinyl acetate	Vinyl acetate is polymerized in the presence of a polyether to produce nonionic emulsifier-free graft copolymers which possess excellent stability to heat, light, mechanical agitation, etc.	*CA*, 57, 2439	485
U. S.	3,035,008	17.6.59		Inter-chemical Corp.	Copolymer of vinyl toluene or styrene with at least one acrylic monomer	(i) 5–30% by wt of a nonalkylic alcohol containing the norbornene nucleus (ii) 70–95% acrylic type ester	Said monomer mixture is polymerized in the presence of the copolymer to form a grafted polymer. Also claimed is a heat curable surface coating composition comprising a volatile organic solvent solution of the grafted polymer and an organic solvent soluble triazine formaldehyde resin or U. F. resin		486

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
Austrl.	59,118/60	Swiss Appl. 18.6.59		Heberlein	Textile fabric, yarn, filament or fiber, paper, plastic film or leather	Perfluoro compounds	A process for modifying the surface of a textile fabric, etc., in which an organic perfluoro compound which contains one or more groups in the molecule activatable by ionizing radiation is grafted to the surface under the influence of such radiation. Irradiation may take place either before or after the application of the perfluoro compound to the surface	487
Brit.	908,224	22.6.59		B. X. Plastics	Poly(ethylene)	Dialkylsebacate	A process for increasing the transparency of poly(ethylene), wherein said monomer is polymerized in the presence of a free radical initiator and at a temperature above the crystalline MP of the poly(ethylene). A synthetic resin such as epoxy or an elastomeric compound such as butyl rubber or chlorinated poly(ethylene) may be incorporated into the composition	488
Ger.	1,092,655	24.6.59		B. A.S.F.	Polymer containing ester or amide groups	Polymerizable monomer	A primary polymer containing ester or amide forming groups is reacted with an azo compound which forms radicals on heating or irradiation, or a hydrazo compound easily oxidized to an azo compound and which contains the corresponding ester or amide group. This modified primary polymer is then used to initiate the graft copolymerization	489

							of an added monomer, if necessary after oxidation of hydrazo groups to azo groups		
Brit.	955,258	U. S. Appl. 14.7.59 20.7.59		Standard Oil	Hydrocarbon copolymer, e.g., isobutylene styrene copolymer	Basic, nitrogen containing ethylenically unsaturated monomer	Said monomer is polymerized in the presence of a substantially saturated hydrocarbon copolymer. The resulting graft copolymer is useful as a lubricating oil additive		490
Brit.	956,556	17.7.59		Koppers	Low mol wt resin, e.g., epoxy, phenolformaldehyde or polyethylene oxide resins	Polymerisable olefinic monomer, e.g., methyl methacrylate styrene	A homogeneous solution of the monomer and resin is heated in the presence of a curing agent. The linear or graft block copolymer so formed is cured to form the desired polymeric material		491
U. S.	3,095,401	20.7.59	25.6.63	Rohm and Haas	Polymer formed from a monovinylidene compound	Vinylthioalkyl unsaturated carboxylate	A transesterification process in which the components are heated at 50–125° in the presence of a suitable catalyst	*CA*, 59, 11687	492
Fr.	1,234,905	31.7.59		Eastman Kodak	Poly(styrene), PVC, poly(isoprene) or C_{4-8} aliphatic monolefinic hydrocarbon polymers	C_{2-18} monoolefin hydrocarbon	A process comprising the polymerization of said monomer in the presence of said polymer and a catalytic mixture consisting of a trialkyl aluminium activated with a titanium halide or an alkyl ester of orthotitanic acid		493
U. S.	3,026,293	6.8.59		Eastman Kodak	Vinyl acrylamide	Monomeric C_{1-8} alkyl acrylate	An alkyl acrylate is polymerized in the presence of an amide polymer and a crosslinking agent selected from divinylbenzene, alkyl acrylate, and dialkyl phthalate		494

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Fr.	1,309,809	7.8.59	15.10.62	Pechiney Compagnie de Produits Chimiques et Electrometallurgiques	Halogenated polymer e.g., PVC	Diolefin having conjugated double bonds, e.g. butadiene	Polymer latex and monomer stirred at 50° in the presence of a radioactive source. After irradiation trinonylphenyl phosphite and a dispersion agent added. Product has improved properties over PVC	*CA*, 58, 14145	495
Brit.	961,940	Fr. Appl. 7.8.59	24.6.64	Pechiney Compagnie de Produits Chimiques et Electrometallurgiques	Equivalent to Fr. 1,309,809		See above		496
U. S.	3,068,187	10.8.59	11.12.62	Minnesota Mining and Manufacturing	Perfluoro polymers	Ethylenically unsaturated monomer, vinyl or vinylidene halides or esters. styrenes, acrylates, vinylcarbazole, butadiene, chloroprene, fluoroprene or isoprene	The monomer is firstly polymerized to about 84% conversion with Bz_2O_2 in dioxane solution, it is then added to the perfluoro polymer and irradiated with UV rays *in vacuo*	*CA*, 58, 5861	497
Brit.	904,262	U. S. Appl. 10.8.59	29.8.62	Minnesota Mining and	Equivalent to U. S. 3,068,187		See above	*CA*, 58, 3576	498

			Manufacturing					
Brit.	879,195	14.8.59	I.C.I.	Poly(propylene)	Diethylamino ethyl methacrylate	Poly(propylene is peroxidized with oxygen and allowed to stand under diethylamino ethyl methacrylate for 12 hr. A composition consisting of the grafted polymer and further isotactic poly(propylene) has good affinity for acid dyes	*CA*, 56, 6187	499
U. S.	3,068,764	19.8.59	Shell	Asphalt	Vinyl monomers	An aqueous dispersion of monomer, in direct contact with an asphalt pavement, is exposed to UV irradiation to form a graft copolymer film of the polymerized monomer with the asphalt surface		500
Brit.	890,267	Ger. Appl. 3.9.59	B.A.S.F.	Polymers from acrylic acid, methacrylic acid or their water soluble solutions, and their amides, acrylic acid esters, acrylonitrile, vinyl esters, vinyl chloride, vinylpyrrolidone, styrene or its derivative, or vinyl methyl ketone	Monomeric unsaturated compounds which contain sulfonic acid and/or phosphoric acid after saponification	A process for the production of water-soluble polymers suitable as sedimentation and filtration acids wherein said monomer is polymerized in aqueous solution and then into the resultant still active primary polymer which has not been removed from its polymerization medium there is polymerized another monomeric unsaturated compound which contains acidic groups		501
U. S.	3,086,959	11.9.59	Dow	Copolymer of *N*-vinyl-2-oxazolidinone and *N*-vinyl lactam	Sulfonic acid compounds	A graft copolymer of from 10–80 wt % of a specified alkenyl group containing organic sulfonic acid compound with 90–20 wt % of said copolymer is claimed		502

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	3,094,504	11.9.59		Dow	Copolymer of *N*-vinyl-3-morpholinone and an *N*-vinyl-heterocyclic compound	Specified alkenyl group containing organic sulfonic acid compound	A graft copolymer of from 10–80 wt % of specified alkenyl group containing organic sulfonic compound with 90–20 wt % of said copolymer is claimed		503
Brit.	896,456 Addition to Brit. 849,063	U. S. Appl. 11.9.59	16.5.62	Dow	*N*-vinyl-3-morpholinone polymer or a copolymer of *N*-vinyl-2-oxazolidone and an *N*-vinyl lactam	Specified monomeric sulfonic acids	Claims graft copolymer in accordance with Brit. 849,063 characterized in that the substrate consists of a preformed *N*-vinyl-3-morpholinone polymer or a preformed copolymer of from 10–9 wt % of *N*-vinyl-2-oxazolidone and from 90–10 wt % of an *N*-vinyl lactam	*CA*. 57, 4887	504
U. S.	3,094,505	28.9.59		Dow	Copolymer of a *N*-vinyl-3-morpholinone and another vinyl-heterocyclic copolymerizable with the above	Vinyl benzyl polyglycol ether	A graft polymer of from 20–80 wt % of a monomeric vinyl benzyl polyglycol ether with 80–20 wt % of said copolymer is claimed		505
U. S.	3,072,599	5.10.59	8.1.63	Dow	Poly(vinyl-3-morpholinone)	Vinyl monomer containing an amino group together with another monomer containing a sulfo group	A graft copolymer of said constituents is prepared by a transfer reaction using $(NH_4)_2S_2O_8$ as initiator. Also claimed is a blend of above graft with poly(acrylonitrile)	*CA*, 58, 14185	506
U. S.	3,072,600	5.10.59		Dow	Copolymer of *N*-vinyl-2-oxazoli-	Mixture of monomers consisting	Patent refers to a composition comprising a polymerized ethy-		507

					done and a *N*-vinyl lactam	of an acrylate and a specified alkenyl group containing organic sulfonic acid compound	lenically unsaturated monomeric material containing at least 80% of polymerized acrylonitrile and a graft copolymer of said copolymer and monomer mixture	
U. S.	3,047,534	7.10.59		Cosden Petroleum Corp.	Rubbery copolymer, e.g., of styrene and butadiene	Styrene	Copolymer is dissolved in monomer and suspended in a hot agitated aqueous bath containing a small quantity of a poly(vinyl alcohol) and a phosphate of calcium, barium, or magnesium	508
U. S.	3,083,176	22.10.59	26.3.63	Dow	Copolymer of N-vinyl-3-morpholinone and another *N*-vinyl heterocyclic compound copolymerizable with the above	Mixture of an acrylamide monomer and a specified alkenyl group containing organic sulfonic acid compound	Patents refers to a composition comprising a polymerized material containing at least 80% of poly(acrylonitrile) and a graft polymer of said constituents	509
U. S.	3,083,177	22.10.59	26.3.63	Dow	Copolymer of *N*-vinyl-2-oxazolidone and a *N*-vinyl lactam	Mixture of a monomeric polyglycol monoester	Patents refers to a composition comprising a polymerized material containing at least 80% of poly(acrylonitrile) and a graft copolymer of said constituents	510
U. S.	3,083,178	22.10.59	26.3.63	Dow	Copolymer of *N*-vinyl-3-morpholinone and another *N*-vinyl heterocyclic compound copolymerizable with the above	Monomeric poly glycol monoester	A graft polymer of from 10–80 wt% of a monomeric polyglycol monoester with 90–20 wt % of said copolymer is claimed	511

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	3,083,179	22.10.59	26.3.63	Dow	Copolymer of *N*-vinyl-2-oxazolidinone and a *N*-vinyl lactam	Mixture of an acrylamide monomer and a specified alkenyl group containing organic sulfonic acid compound	Patent refers to a composition comprising at least 80% of poly(acrylonitrile) and a graft polymer of said constituents		512
U. S.	3,075,948	23.10.59	29.1.63	Owens-Illinois Glass Co.	Homo- and copolymers of polyolefins	Unsaturated silane, e.g., vinyl silane or vinyl triethoxysilane	Certain unsaturated silanes are grafted onto polyolefins using a solution technique and a free radical forming catalyst at 100–300°C	*CA*, 58, 10326	513
U. S.	3,082,186	4.11.59		Dow	Copolymer of *N*-vinyl-3-morpholinone and another *N*-vinyl heterocyclic compound copolymerizable with the above	Monomeric aminoethyl acrylates	A graft polymer of from 20–80 wt % of a monomeric aminoethylacrylate compound with 80–20 wt % of said copolymer is claimed		514
U. S.	3,084,138	4.11.59		Dow	Copolymer of *N*-vinyl-2-oxazolidone and a *N*-vinyl lactam	Monomeric acrylate	Patent refers to a composition comprising at least 80% of poly(acrylonitrile) and a graft polymer of said constituents		515
Brit.	952,639 Addition to Brit. 851,491	U. S. Appl. 9.11.59		Monsanto	Copolymer of butadiene and styrene	Mixed of styrene and acrylonitrile	Monomer mixture is polymerized in the presence of a latex of said copolymer and optionally a polyolefinic crosslinking agent. Also claims a blend of above grafted polymer and a butadiene-styrene copolymer		516

Fr.	Fr. Addition 77,839 to Fr. 1,180,764	U. S. Appl. 9.11.59		Monsanto	Equivalent to Brit. 952,639		See above		517
U. S.	3,073,798	9.11.59	1.5.63	Monsanto	Copolymers of butadiene and styrene	Mixture of styrene and acrylonitrile	Claims a blend of a styrene-acrylonitrile/butadiene-styrene graft copolymer and a styrene-acrylonitrile interpolymer both prepared by emulsion polymerization, which is moulded into articles with improved optical clarity and surface finish	*CA*, 58, 12736	518
Japan	17,634(61)	28.11.59	28.9.61	Toyo Rayon	Viscose-rayon	Acrylonitrile	Viscose-rayon fiber is soaked in an acidified potassium permanganate solution then washed thoroughly in water and soaked in acrylonitrile (oxygen free) at 45° for 5 hr to form a graft copolymer	*CA*, 56, 14485	519
Japan	13,787(62)	18.12.59	12.9.62	Toyo Rayon	(Process claim)		Grafted yarns of synthetic polymers are usually washed with solvents (I) that dissolve monomers and oligomers not grafted to the yarns. However, the yarns often adhere to each other during drying. This difficulty is improved by washing the grafted yarns with I and then with a solvent which does not dissolve the oligomers but is miscible with I. Thus nylon yarn, irradiated in styrene-MeOH-H_2O is washed with C_6H_6, MeCOEt, or dioxane and then with MeOH and dried	*CA*, 59, 7706	520

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Germ.	1,105,179	19.12.59		Farbwerke-Hoechst	Polyalkylene glycols	Olefins especially olefins containing nitrogen, e.g., acrylonitrile	Olefins are radically polymerized in aqueous media in the presence of a polyalkylene glycol which is insoluble or slightly soluble in water but miscible in the monomer. Radiation may also be used to initiate polymerization	*CA*, 56, 3662	521
Brit.	967,332	Germ. Appl. 19.12.59		Farbwerke-Hoechst	Equivalent to Germ. 1,105,179		See above		522
U. S.	3,098,838	22.12.59		National Starch and Chemical Corp.	Poly(vinyl ethyl ether)	Vinyl acetate	Solution polymerization of vinyl acetate with the aid of a catalyst in the presence of poly(vinyl ethyl ether); the latter being dissolved in an organic solvent		523
Ger.	1,110,419	28.12.59		Farbwerke Hoechst	Poly alkylene glycol	Vinyl, acrylic or methacrylic esters	Said monomer is polymerized in the presence of a poly alkylene glycol with a free radical activator such as diacetyl peroxide which need not be removed from the end product		524
U. S.	3,100,758	31.12.59		Continental Can Co.	Vinyl halide polymer	Oxirane containing monomer, e.g., glycidyl acrylate	Polymer dissolved in an organic solvent is heated with monomer in the presence of a free radical polymerization catalyst		525
Ger.	1,111,394	5.1.60		Hoechst	Polyalkylene glycols	Olefins unsaturated monomers	Olefinic monomers are polymerized in the presence of a polyalkylene glycol and an organic solvent, with the exclusion of H_2O, by a free radical catalyst or by irradiation	*CA*, 56, 3647	526

Ger.	1,111,391	7.1.60		B.A.S.F.	*N*-nitrosated copolymers	Olefinically unsaturated monomers	Copolymers of olefinic unsaturated aliphatic cycloaliphatic or heterocyclic acrylamides which have the amide-*N* mono-substituted by alkyl, alkenyl, aralkyl, cycloalkyl, or cycloalkenyl groups are nitrosated and then treated with said monomers	*CA*, 56, 3659	527
Brit.	899,567	Ger. Appl. 7.1.60	27.6.62	B.A.S.F.	Polycondensates containing CONH groups	Olefinic monomers	Graft copolymers can be made from polycondensates containing CONH groups by nitrosation of the amide-*N* groups and copolymerization with olefinic monomers	*CA*, 57, 7474	528
Brit.	891,758	Ger. Appl. 7.1.60		B.A.S.F.	Nitrosated copolymers	Olefinically unsaturated monomers	Nitrosated copolymers are reacted with olefinically unsaturated monomers to form graft copolymers		529
Ger.	1,138,934	7.1.60		B.A.S.F.	Polyamides	Vinyl monomers	Polyamides are nitrosated with for example nitrosyl chloride and then reacted with vinyl monomers. The latter reaction may be initiated thermally, photochemically or by traces of alkali and/or salts of transition metals		530
Japan	17,993(61)	12.1.60	30.9.61	Toyo Rayon Co.	Reductive polymers	Monomers containing double bonds	The treatment of a reductive polymer with a monomer containing a double bond at pH 3.5 in the presence of permanganate is described.	*CA*, 57, 1087	531
Belg.	586,455	12.1.60	30.11.61	Solvay-Cie	Polymers containing —ONO_2 or —ONO groups	Styrene, acrylonitrile, vinyl chloride, or methyl methacrylate	Polymers containing ONO_2 or ONO groups are used to initiate copolymerisation with said monomers at the decomposing —ONO_2 group with little formation of homopolymer	*CA*, 57, 2439	532

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	899,993	Belg. Appl. 12.1.60		Solvay-Cie	Equivalent to Belg. 586,455		See above		533
Germ.	1,118,548	Belg. Appl. 12.1.60		Solvay-Cie	Equivalent to Belg. 586,455		See above		534
Fr.	1,255,077	20.1.60		Polyplastic	Polyolefin, e.g., poly(ethylene) or poly(propylene)	Acrylic acid or a mixture of styrene and acrylic acid, maleic anhydride or itaconic acid, or a mixture of α-crotonic acid and vinyl acetate	Carboxylic acid or anhydride groups are grafted onto a polyolefin in a ratio of 0.01–5 meg. acid/g of polyolefin and the resulting graft copolymer is treated with reagents which undergo condensation with the acid groups. For example poly(ethylene) is ozonized and grafted with a mixture of α-crotonic acid and vinyl acetate. The product is then crosslinked with succinamide	*CA*, 56, 7506	535
Brit.	964,977	Fr. Appl. 1.2.60		Polyplastic	Polyolefin, e.g., poly(ethylene) or poly(propylene); [cf. Fr. 1,255,077 (see above)]	Ethylenically unsaturated carboxylic acid or anhydride	Claims a method of covering a metal surface comprising applying to the surface a modified polyolefin comprising a polyolefin which has had grafted thereon from 0.01–5meq/g of an ethylenically unsaturated carboxylic acid or an ethylenically unsaturated carboxylic acid anhydride		536
Fr.	1,278,574	Germ. Appl. 3.2.60		B.A.S.F.	Copolymers of monosubstituted acrylamides with	Unsaturated monomers	The copolymers are nitrosated on the amide N atom at temperatures between −20 and +75°C and		537

					unsaturated monomers		then reacted with unsaturated monomers at temperatures between −30 and +150°C under the influence of light of wavelength 1800–7000 A		
Brit.	887,887	U. S. Appl. 10.2.60	24.1.62	W. R. Grace	Halogen-containing polymer in which some of the halogen atoms may be removed by reaction with an alkali metal or an alkali metal hydrocarbon	A monomer capable of forming living polymer by an anionic mechanism	The monomer is polymerized in the presence of a catalyst having the general formula R. M. (where R is alkyl, aryl aralkyl and M is an alkali metal especially Li) and then mixed with the halogen-containing polymer	*CA*, 57, 1088	538
U. S.	3,136,738 continuation in part of U. S. 3,017,391	10.2.60	9.6.64	Monsanto	A linear carbon-to-carbon polymer derived by the addition polymerisation of one or more ethylenic monomers said polymer containing at least one *N*.*N*-diacyltertiary amidegrouping, e.g., ethylene/maleic anhydride, styrene/*N*-methacrylcaprolactam or styrene-*N*-methacrylyl chloride copolymer	A lactam, e.g., ε-caprolactam	Claims graft copolymers of polyamides onto certain polymeric substrates (as defined) which have a greater resistance to solvents than the polylactams alone or the ethylenic polymers alone or of physical blends of the two	*CA*, 61, 5813	539
Brit.	973,567	U. S. Appl. 10.2.60	28.10.64	Monsanto	Equivalent to U. S. 3,136,738		See above		540

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	3,057,816	12.2.60	9.10.62	Dow	Copolymer of *N*-vinyl-2-oxazolidinone and *N*-vinyl lactam	Acrylamide, methacrylamide	$K_2S_2O_8$ is used to initiate the graft copolymerization	*CA*, 58, 1561	541
U. S.	3,057,817	12.2.60	9.10.62	Dow	Monoethylenically unsaturated. Monomer containing > 10% by wt *N*-vinyl-3-morpholinone	Acrylamide	$K_2S_2O_8$ is used to initiate the graft copolymerization	*CA*, 58, 1561	542
U. S.	3,097,186	29.2.60		Dow	Copolymer of butadiene and isopropenylbiphenyl or vinyl biphenyl	Monovinyl aromatic hydrocarbon, e.g., styrene	Grafting by transfer, using a free radical initiator		543
U. S.	3,179,485	Japan Appl. 2.3.60		Shin Nippon Chisso Hiryo Kabushiki Kaisha, Osaka	Poly(propylene)	Vinyl monomer having epoxy groups, e.g., glycidyl methacrylate or glycidylurethane	Poly(propylene) fibers are rendered readily dyeable by treatment with UV radiation in the presence of a sensitizer, graft polymerizing with a vinyl monomer having epoxy groups and then treating the fibers with an aqueous solution containing oxyamines or sodium salts of aminoacids and dimethyl formamide		544
Brit.	929,245	U. S. Appl. 3.3.60		Dow	Poly(*N*-vinyl-3-morpholinone)	Acrylonitrile	The polymeric substrate is dissolved in a solvent for poly(acrylonitrile) and reacted with monomer in the presence of a suitable catalyst		545
Fr.	1,258,434	4.3.60		Rhone-Poulenc	Poly(vinyl chloride) or vinyl chloride-	Butadiene (1:3)	Butadiene is grafted onto PVC by a transfer process initiated by free		546

					vinyl acetate copolymer		radical catalysts		
U. S.	3,119,786	Fr. Appl. 4.3.60	28.1.64	Rhone-Poulenc	Equivalent to Fr. 1,258,434		See above		547
Brit.	897,341	Fr. Appl. 4.3.60 8.11.60	23.5.62	Rhone-Poulenc	Equivalent to Fr. 1,258,434		See above		548
U. S.	3,144,426	4.3.60	11.8.64	O. W. Burke, Jr.	Butyl rubber copolymers	Ethylenically unsaturated monomer, e.g., methyl methacrylate	A method is described for preparing aqueous dispersions of copolymers such as butyl rubbers. The copolymer solution in a suitable solvent is partially halogenated, emulsified in water, the solvent removed from the emulsion and a monomer added. The monomer has at least one ethylenically unsaturated group and may, for instance, be a methacrylate	*CA*, 61, 12175	549
Brit.	975,421	U. S. Appl. 7.3.60	18.11.64	Rohm and Haas	Poly(alkyl acrylate)	Alkyl methacrylate	Graft copolymers are prepared by polymerizing an alykl methacrylate while in intimate contact with a preformed poly(alkyl acrylate). Also claims blends of the above graft copolymers with vinyl halide polymers, e.g., PVC		550
Brit.	916,529	Japan Appl. 10.3.60		Kabushiki Kaisha Hitachi Seisakusho	Natural or synthetic macromolecular substance, e.g., poly-α-olefin, poly-vinyls, polyesters, etc.	Monomer containing an epoxy group and a polymerizable double bond, e.g., glycidyl methacrylate	The polymer is treated with said monomer and then with a compound which has a functional group containing active hydrogen and capable of opening up the epoxy group		551

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Japan	13,881(62)	14.3.60	13.9.62	Toyo Spinning Co.	Polymers having OH, CO, CHO, SH, or NH_2 groups	Monomers which undergo radical polymerization	Grafting is carried out in the presence of uranium salts (with UV irradiation if necessary).	*CA*, **59**, 7671	552
Brit.	899,029	Germ. Appl. 24.3.60		Chemische Werke Hüls	Poly(butadiene)	Vinyl chloride or a vinyl chloride copolymer	Vinyl chloride is polymerized with a free radical initiator in an aqueous suspension of poly(butadiene)		553
Fr.	1,284,280	Germ. Appl. 24.3.60		Chemische Werke Hüls	Equivalent to Brit. 899,029		See above		554
Japan	9,837('62)	26.3.60	31.7.62	Showa Electric Industry Co.	Poly(ethylene)	Styrene	Poly(ethylene) is irradiated in air with Co^{60} to a specified dose, immersed in styrene, heated at 70° for 16 hr, washed with benzene and reirradiated in air or preferably *in vacuo*	*CA*, **60**, 13342	555
Japan	690('62)	30.3.60	29.3.62	Toyo Spinning Co.	Poly-α-olefins	Vinyl monomers	Vinyl monomers are grafted onto poly α-olefins in the presence of water by irradiating *in vacuo* with UV light	*CA*, **58**, 12732	556
Japan	8,733('62)	31.3.60	19.7.62	Toyo Spinning Co.	Polymeric alcohols, aldehydes, ketones, and amines	Vinyl monomers	Vinyl monomers are grafted on said polymers in the presence of HClO, HBrO or their salts at 20–60° preferably with UV irradiation.	*CA*, **58**, 11533	557
Japan	8,735('62)						Vinyl monomers are grafted onto the same polymers in the presence of transition metal compound and oxygen		558

Brit.	913,370	15.4.60 19.1.61 27.1.61 9.2.61 20.2.61 27.3.61		A. D. Little Inc.	Wool-polyamide, polyurethane, polyurea, polyester, or polycarbonate		Claims wool having grafted thereto a condensation polymer formed *in situ*. The polymer may be a polyamide, polyurethane, polyurea, polyester, polycarbonate, or an interpolymer wherein the recurring units contain 2 or more different units of amide, urethane, urea, ester, or carbonate		559
Austrian	223,820	20.4.60	10.10.62	Werner H. Kreidl	Styrene, saturated acrylic or methacrylic acid esters, acrylonitrile, vinyl pyridine, copolymerized with alkyl acrylates, methacrylates, methalkyl acrylates, and *sym*-divinyl compounds	Fatty acid vinyl esters, alkyl esters, or *N*-vinylpyrolidinone	Covers graft copolymers prepared from monomers with considerably different copolymerization parameters	*CA*, 58, 1555	560
Brit.	903,566	U. S. Appl. 29.4.60		Du Pont	Poly(ethylene,) poly(propylene.) poly(vinyl fluoride), or a polyamide	Ethylene or butadiene	A mixture of an olefin and SO_2 is contacted with a solid organic polymer having a mol wt. ≥ 5000 previously activated by irradiation. The irradiation may also be effected while the polymeric substrate is in contact with the olefin SO_2 mixture		561
Belg.	603,086	U. S. Appl. 29.4.60		Du Pont	Euqivalent to Brit. 903,566		See above		562
Fr.	1,293,597	U. S. Appl. 29.4.60		Du Pont	Equivalent to Brit. 903,566		See above		563

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	962,575	Fr. Appl. 13.5.60		Polyplastic and Kleber Colombes	Film or fabric of poly(ethylene glycol)	Polar, vinylidonic monomer	Claims a process for grafting a monomer to linear polyesters by a preozonization method		564
Japan	11,437(62)	26.5.60	18.8.62	Showa Electric Industry Co.	Poly(ethylene), poly(tetrafluoroethylene)	Vinyl monomers	The polymer is first preirradiated in air with γ-rays from Co^{60}, then dipped in the monomer and further irradiated with UV light at less than 30°C.	*CA*, 59, 780	565
U. S.	3,170,892	29.5.60	23.2.65	Du Pont	Poly(ethylene)	Sulfur dioxide	Poly(ethylene) film is irradiated *in vacuo* at −78°C with 2 Mev. electrons and then exposed to a 1:1 molar mixture of benzene and sulfur dioxide at 25° for 20 hr. The grafted film showed improved adhesion for printing ink	*CA*, 62, 10635	566
Austrl.	2,071/61	U. S. Appl. 31.5.60 2.3.61		United States Rubber	(Process claim)		Claims a method of forming a graft copolymer comprising exposing a base polymer to high energy causing radiation either before or after immersing the said base polymer in a liquid monomer, characterized by the step of adding to the monomer a catalytic diluent which is a solvent for the monomer but a nonsolvent for the homopolymer		567
Japan	18,900(62)	31.5.60	21.12.62	Nihon Hoshasen Kobunshi Kenkyn Kyokai	Cellulose	Monomer capable of radical polymerization	The cellulose is first irradiated in methyl alcohol with γ-rays in the absence of air. The MeOH is then evaporated, monomer added and the tube sealed *in vacuo* and heated at 50° for 20 hr	*CA*, 59, 7700	568

Belg.	596,692	U. S. Appl. 4.6.60		W. R. Grace and Co.	Poly(ethylene)	Styrene	A graft copolymer is prepared by homogenizing a mixture of polyethylene, styrene monomer and a peroxide in the absence of a liquid medium at a temperature at least as high as the softening point of the poly(ethylene) styrene mixture		569
Brit.	983,587	Germ. Appl. 4.6.60	17.2.65	Farbwerke Hoechst	1,2-epoxy hydrocarbon polymer, e.g., poly(ethylene glycol)	Unsaturated organic compound, e.g., vinyl acetate	Modified 1,2-epoxy hydrocarbon polymers are prepared by grafting an unsaturated organic compound onto a hydrocarbon polymer using a free radical catalyst	*CA*, 62, 13271	570
Brit.	867,822	7.6.60		Shell Research Ltd.	Conjugated diene polymer or a copolymer containing at least 80% by wt of a conjugated diene	Acrylonitrile, and styrene	The monomer mixture is polymerized in aqueous emulsion in the presence of an aqueous latex of a conjugated diene polymer, an alkyl mercaptan and a radical addition polymerization initiator		571
Belg.	605,139	Germ. Appl. 18.6.60		Hoechst	1,2-epoxy polymer	Chlorinated monomer, e.g., vinyl chloride or vinylidene chloride	The chlorinated monomer is polymerized in the presence of the epoxy polymer by a free radical initiator. The components in specified proportions are dissolved in an appropriate solvent		572
Ital.	640,015	30.6.60	21.5.62	Montecatini	Amorphous noncrystallizible linear α-olefin copolymers or copolymers of α-olefins with each other and/or with ethylene	Styrene, butadiene, or isoprene	An aqueous suspension of said polymers or copolymers is subjected, under a pressure between 1 and 20 atm. and at a temperature between 40 and 200°C to the action of molecular oxygen. The peroxide groups thus formed are used to initiate graft copolymerization of added monomer	*CA*, 59, 4114	573
Belg.	605,552	Ital. Appl. 30.6.60		Montecatini	Equivalent to Ital. 640,015		See above		574

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	905,624	Ital. Appl. 30.6.60		Montecatini	Equivalent to Ital. 640,015		See above		575
Fr.	1,261,808	6.7.60		Monsanto	Rubbery polymer containing in the chemically bound state at least 85% of a conjugated 1,3-diene	Monovinylidene aromatic hydrocarbon possibly halogenated in the ring and acrylonitrile methacrylonitrile or a mixture of such nitriles	The monomer mixture is polymerized in the presence of an aqueous dispersion of a rubbery polymer and not more than 1.5% of a cross linking monomer having several nonconjugated terminal ethylenic groups		576
Germ.	1,137,555	8.7.60	4.10.62	Kulzer and Co.	Copolymers of hexafluoropropylene and vinylidene fluoride	Monomeric vinylic or acrylic compounds especially acrylates or methacrylates	The copolymer is dissolved in the monomer and polymerized by addition of peroxidic catalysts or peroxidic redox systems. Bead polymers of the monomers used may be added	*CA*, 58, 8111	577
U. S.	3,110,695	15.7.60	12.11.63	Koppers	Poly(ethylene oxide)	Methyl methacrylate	Graft copolymers are prepared by dissolving a low mol wt resin in a polymerizable olefinic monomer and polymerizing by free radicals initiated in the monomer. Depending upon the initiator used, its concentration and the polymer/monomer system, the application of heat to initiate polymerization may or may not be necessary		578
Japan	2,315('64)	16.7.60	6.3.64	Asahi Chemical Industry	Poly(acrylonitrile)	Methyl methacrylate	Poly(acrylonitrile) fiber previously heated with hydroxylamine is warmed at 60° for 3 hr with MeM, acetone, VCl_2, and HCl in a nitro-	*CA*, 61, 1999	579

							gen atmosphere to yield a graft copolymer		
U. S.	3,187,067	20.7.60		Standard Oil	Copolymer of styrene and monobromostyrene	α-olefin, e.g., ethylene	A copolymer of styrene and monobromostyrene in an inert hydrocarbon medium is reacted with an alkali or alkaline earth metal to form a polymeric organometallic compound. Said polymeric compound is then treated with an α-olefin in the presence of a co-catalyst comprising a salt of a metal of Group IVa, Va, or VIa to form a graft copolymer		580
U. S.	3,133,825	20.7.60	19.5.64	Dow	Vinyl chloride polymers, e.g., PVC	Mixture of two ethylenic monomers, e.g., styrene and a vinyl ester	Claims polymer compositions prepared by dispersing a finely divided vinyl chloride polymer in a mixture of two monomers and subjecting the resultant mixture to high energy ionizing radiation. Before irradiation the mixture can be applied to a fibrous material		581
U. S.	3,143,521	21.7.60	4.8.64	W. R. Grace	Halogenated polyolefins	Monomer mixture selected from monoethylenically unsaturated aromatic hydrocarbons and maleic acid, acrylic acid, methacrylic acid, cinnamic acid and the anhydrides, metal salts, and nitriles of said acids	Halogenated polyolefins irradiated and subsequently oriented are graft-copolymerized with styrene and maleic anhydride	*CA*, 61, 13501	582

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	927,519	U. S. Appl. 2.8.60 21.2.61	29.5.63	W. R. Grace	Poly(ethylene)	"Vinylidene" compound	Poly(ethylene) is crosslinked by irradiation under nitrogen in a Van de Graaff accelerator and heated with the monomer at 78° in an N atm. for 2 hr. Addition of 0.01–20% (wt) of the grafted product to the untreated poly(ethylene) increases the clarity from 2–10-fold	*CA*, 59, 6591	583
Germ.	1,138,227	2.8.60		B.A.S.F.	High mol wt compounds containing metal atoms, metal hydrides, or a metal-organic group linked via a metal-C-bond	Ethylenic or acetylenic monomers	The method is particularly applicable to the grafting of stereospecific polyolefin side chains onto the reaction product of diethyl aluminium hydride and an unsaturated copolymer (e.g., of styrene and butadiene) the reaction being carried out in the presence of $TiCl_4$		584
Brit.	948,747	3.8.60		Cosden Petroleum Corp.	Styrene-butadiene rubber	Styrene	Claims a process for producing beads by the polymerization of an aqueous suspension of a monomer in a solution of a preformed polymer containing finely divided solid particles of calcium, barium or magnesium phosphate and either a monomer soluble phospholoid or poly(vinyl alcohol) or both		585
Brit.	932,852	4.8.60	31.7.63	B. X. Plastics	Poly(vinyl chloride) or a vinyl chloride copolymer	Conjugated diolefin and at least one copolymerisable vinyl monomer, e.g., butadiene and	Claims a blend comprising a homopolymer or copolymer of vinyl chloride and a rubbery copolymer of said constituents. The blends may contain a plasticizer and an additional polymeric consti-		586

						acrylonitrile or butadiene and methyl methacrylate	tuent. Improved processability, transparency, and tensile strength are achieved in these blends, while retaining the high impact strength of graft copolymer	
Belg.	606,944	Germ. Appl. 4.8.60 6.8.60 8.10.60		B.A.S.F.	Polycondensates and polyolefins	Olefinic monomers	Production of graft copolymers in the mass from polycondensates and polyolefins by reacting in the molten state, polycondensates comprising carbonamide groups that have been partially or completely converted into N-nitroso groups, with polyolefins and optionally with monomers having olefinic bonds. Also claims homogeneous mixtures of polyolefins with above formed grafts polymers	587
Brit.	993,413	Germ. Appl. 4.8.60	26.5.65	Hibernia-Chemie	Isotactic poly(propylene)	A mixture of propylene and another copolymerizable monomer	Claims a polymeric product comprising a major proportion of isotactic poly(propylene) and a minor proportion of a copolymer of propylene and at least one olefin other than propylene, having 4 or less carbon atoms, in which at least part of the copolymer is grafted onto the poly(propylene)	588
Brit.	946,065	U. S. Appl. 8.8.60		Esso Research and Engineering	Butyl rubber or an ethylene, 1-butene copolymer	Acrylic acid ester	A solution of the polymer in an inert organic solvent is reacted with a hydroperoxide, an aldehyde or aldehyde forming substance or a mercaptan, in the presence of oxygen to obtain an intermediate activated polymer. This polymer is then heated with the monomer to form a graft copolymer	589

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Belg.	607,015	U. S. Appl. 8.8.60		Esso Research and Engineering	Equivalent to Brit. 946,065		See above		590
Germ.	1,134,201	9.8.60	28.2.63	V.E.B. Chemische Werke Buna	Poly(vinyl chloride)-poly(butadiene)		Modified plastics are prepared by kneading at −20 to +20°C a plastomer, e.g., PVC with 1–5% swollen elastomers, e.g., poly(butadiene) in an organic solvent, e.g., benzene. The solvent is then removed by heating *in vacuo*	*CA*, 57, 10045	591
Japan	2,138('63)	12.8.60	14.3.63	Toyo Rayon Co. Ltd.	Solid high mol wt polyolefins	Vinyl acetate	Vinyl acetate emulsion are effective for graft copolymerisation with solid high mol wt olefins	*CA*, 57, 4059	592
Austrl.	63,545/60	12.8.60		Polyplastic	(Process claim)		Production of graft copolymers by submitting a backbone polymer to the action of ozone, said backbone polymer being dispersed in a liquid which does not immediately dissolve it, whereafter the ozonized polymer is decomposed in the presence of monomers, the system being completely free of any additional polymerization catalyst other than ozonized polymer itself		593
U. S.	3,180,908	12.8.60	27.4.65	General Tire and Rubber	Poly(vinyl chloride)	Styrene-acrylonitrile mixtures	The grafting of styrene-acrylonitrile mixtures to suspension polymerized vinyl chloride yields products which are superior for thermoforming into flexible sheets by	*CA*, 63, 3140	594

							virtue of their enhanced tear strength and elongation		
Brit.	994,342	U. S. Appl. 12.8.60	2.6.65	General Tire and Rubber	Equivalent to U. S. 3,180,908		See above		595
Belg.	607,122	U. S. Appl. 12.8.60		General Tire and Rubber	Equivalent to U. S. 3,180,908		See above		596
Belg.	607,269	Germ. Appl. 17.8.60		Hoechst	Poly(ethylene), poly(propylene) or copolymers of ethylene and propylene	Low mol wt modifiers optionally containing groups that are still reactive after grafting	Said polymer is treated with a free-radical generator in the presence of an inert solvent and a modifier of low mol wt acting as an acceptor of electrons and preferably containing a C=C or C=O bond, said modifier being capable of reacting with the activated macromolecules but not with the free radical generator under the conditions used		597
Japan	7,876('63)	20.8.60	3.6.63	Toyo Spinning Co.	Cellulose	Acrylonitrile	Viscose-rayon is soaked in a saturated solution of acrylonitrile, glyoxal is added and the mixture is irradiated with UV light at 40° for 5 hr	*CA*, **59**, 7704	598
Japan	26,300(63)	27.8.60	13.12.63	Asahi Chemical Industry Co.	Cellulose	Methyl methacrylate	A mixture of methyl methacrylate, acetone, water, and $(NH_4)_2S_2O_8$ at 25° is added to the cellulose and heated in N for 2 hr	*CA*, **60**, 5695	599
Japan	10,427(65)	3.9.60	26.5.65	Kureha Spinning	Cellulose, wool or poly(vinyl alcohol)	Styrene or methacrylate	Modified fibers of cellulose, wool or poly(vinyl alcohol) are obtained by graft copolymerizing with styrene or methacrylates in the presence of water soluble ferric salts as catalyst	*CA*, **63**, 16523	600

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	980,258	8.9.60	13.1.65	Natural Rubber Producers' Research Association	Natural or synthetic rubber	Vinyl or vinylidene monomer	Claims a process for the production of a modified rubber comprising successively polymerising a plurality of separately added increments of a vinyl or vinylidene monomer in a latex of a natural or synthetic rubber using an organic peroxide as initiator, said monomer being polymerizable in the presence of said latex and each of said increments being substantially completely polymerized before the next succeeding increment is added		601
Brit.	999,100	Germ. Appl. 4.10.60	21.7.65	Farbwerke Hoechst	1,2-epoxyhydrocarbon polymer, e.g., poly(ethylene glycol) or poly(propylene glycol)	Olefinically unsaturated compound, e.g., α,β-unsaturated dicarboxylic acid	Claims a process for the manufacture of chemically modified 1,2-epoxy hydrocarbon polymers comprising reacting said polymers in the presence of a free radical catalyst with at least one olefinically unsaturated monomer		602
Germ.	1,131,883	7.10.60	20.6.62	B.A.S.F.	Block copolymers (I) from polyolefins, poly(styrene), or their copolymers	Carboxamide group containing polycondensates (II)	The I and II are homogenized in the presence of radical forming catalysts at 50–300° by using high shearing stresses and velocity gradients	*CA*, 57, 8749	603
Brit.	927,968	Germ. Appl. 7.10.60		B.A.S.F.	Equivalent to Germ. 1,131,883		See above		604
U. S.	3,177,269	10.10.60	6.4.65	Dow	Polyolefin, e.g., poly(ethylene), poly(propylene), or copolymers of	Methacrylic acid	Graft copolymers of polyolefins and methacrylic acid are prepared by heat plasticizing a polyolefin, adding monomeric methacrylic acid	*CA*, 62, 16462	605

					these		having dissolved in it up to 5% of an organic peroxide or similar compound having a half-life of at least 15 min, and heating for a sufficient time at 110–250°C		
U.S.	3,177,270	10.10.60	6.4.65	Dow	Polyolefins	Monovinyl aromatic hydrocarbon or a nuclear halogenated monovinyl aromatic hydrocarbon	In a process similar to that described in U.S. 3,177,269, the monomer to be grafted may be a monovinyl aromatic hydrocarbon or a nuclear halogenated monovinyl aromatic hydrocarbon of the benzene series or a mixture of these with a minor proportion of an acrylic monomer such as (meth)acrylonitrile, (meth)acrylic acid, or maleic anhydride	*CA*, 63, 1953	606
Fr.	1,276,804	14.10.60	8.3.62	Pechiney Compagnie de Produits Chimiques et Electrometallugiques	Vinyl polymers	Butadiene	Graft copolymerization of butadiene onto $K_2S_2O_8$ polymerized vinyl polymer backbones in emulsion is catalyzed by heavy metal complexing agents	*CA*, 57, 11401	607
Brit.	954,041	19.10.60 6.7.61	2.4.64	I.C.I.	Polysiloxanes	Monohydric alcohols, e.g., polyether alcohols	Siloxane-oxyalkylene graft copolymers in which the oxy- or poly(oxyalkylene) groups are attached to Si are obtained by reaction of polysiloxanes containing Si-bonded hydrogen with monohydric alcohols. Alkali metal alkoxides or metal salts which are soluble in the reaction mixture are effective catalysts. The products are useful as additives in the manufacture of polyurethane foams	*CA*, 61, 5815	608

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Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	951,274	Germ. Appl. 22.10.60 22.3.61	4.3.64	Rohm and Haas	Copolymer of butadiene and styrene	Methyl methacrylate	A process for the production of molding compositions which comprises polymerizing methyl methacrylate in the presence of a copolymer of butadiene and styrene	*CA*, 60, 16063	609
Brit.	997,093	25.10.60	30.6.65	Courtaulds	Hydrocarbon polymer, e.g., poly(ethylene) or poly(propylene)	Acrylonitrile or methacrylic acid	Claims a process for modifying the surface properties of a hydrocarbon polymer by graft polymerization, comprising forming free radicals on the surface of the polymer by subjecting the polymer to an electric discharge in a gas at a pressure of up to 1 mm Hg, subsequently contacting the polymer with a polymerizable substance and initiating the graft polymerization of the substance on the polymer by free radicals on the surface of the polymer	*CA*, 63, 7157	610
Brit.	971,778	Ital. Appl. 26.10.60	7.10.64	Montecatini	Poly(propylene)	Mixture comprising glycidyl methacrylate, or the glycidyl ester of hydroxyalky.-vinyl ether and acrylic acid, acrylamide, methacrylic acid, methcrylamide, maleic or itaconic acid, or amides thereof	Claims a process of applying a subbing layer to a crystalline olefin polymer film comprising treating the film with said monomer mixture, contacting the treated film with a layer of gelatine and irradiating the resultant composite film with UV light so as to graft copolymerize the monomer mixture thus realizing the adhesion of the gelatine to the film		611

Japan	7,134('63)	5.11.60	27.5.63	Toyo Spinning Co.	Poly(propylene)	Vinyl monomers having basic nitrogen atoms	Graft copolymerization of vinyl compounds having basic *N* atoms onto poly(propylene) is accomplished in the presence of methyl methacrylate, methyl acrylate, or styrene (in their mixtures) and vinyl compounds having carboxyl or sulfoxyl groups. The products have good dyeability	*CA*, 60, 16043	612
Fr.	1,283,856	7.11.60	18.6.62	Polyplastic	Inert polymer, e.g., poly(ethylene)	Polymerizable monomer	Grafting is initiated by ozonation, polymer is then coated with an adhesive composition compatible with it to form an integral laminate	*CA*, 57, 15376	613
Fr.	79,558 Addn. to Fr. 1,258,434	8.11.60		Rhone-Poulenc	Vinyl chloride-vinyl acetate copolymer	Butadiene	Thermoplastic, highly resilient composition are based on a graft polymer of said copolymer with 1–20% butadiene. Polymerization is carried out in aqueous dispersion		614
Japan	1,249('63)	11.11.60	19.2.63	Japan Radiation High Polymer Research Assn.	Cellulose	Vinyl monomers	A mixture of cellulose and monomer is emulsified with surfactant and irradiated in air with γ-rays	*CA*, 59, 8928	615
Brit.	920,867	U. S. Appl. 16.11.60		General Aniline and Film Corp.	Polymeric *N*-vinyl lactam substrate	Styrene	A mixture of styrene monomer or a water insoluble homolog thereof in an aqueous solution of a polymeric *N*-vinyl lactam is subjected to polymerization conditions in the presence of a free radical supplying catalyst		616

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Germ.	1,156,238	U. S. Appl. 16.11.60	24.10.63	General Aniline and Film Corp.	Polymeric *N*-vinyl lactam substances	Acrylic esters	Acrylic esters are grafted to water soluble poly(*N*-vinyl lactams) by emulsion polymerization	*CA*, 60, 14706	617
Germ.	1,156,985	U. S. Appl. 16.11.60	7.11.63	General Aniline and Film Corp.	Equivalent to Brit. 930, 867		See above	CA, 60, 1905	618
Brit.	947,800	U. S. Appl. 25.11.60		Shell	Claims polymeric lubricating oil additives consisting of a linear carbon backbone chain and attached thereto long chain alkyl and alkylene ester groups				619
Japan	18,562(63)	25.11.60	17.9.63	Toyo Spinning Co.	Poly(ethylenimine)	Mixture of acrylamide and ethyl acrylate	Acrylamide and ethyl acrylate are mixed with poly(ethylenimine) and heated at 70° for 30 min. The resulting graft copolymer emulsion is added to cellulose	*CA*, 60, 3151	620
U. S.	3,157,460	25.11.60	17.11.64	United States Department of Agriculture	Cyanoethylated cotton fiber yarn	Acrylonitrile	Cyanoethylated cotton fiber yarn is treated with an aqueous solution of acrylonitrile and zinc chloride and irradiated by high energy radiation to graft copolymerize the acrylonitrile onto the fiber	*CA*, 62, 4159	621
Japan	11,237(62)	29.11.60	16.8.62	Asahi Chemical Industry Co.	Polymers containing hydroxyl groups	Vinyl monomers	Grafting of vinyl monomers onto polymers containing OH groups is effectively carried out by treating a polymer in which some of the OH groups are converted to amide oxime groups through cyanoethylation	*CA*, 59, 1813	622
Japan	13,887(62)	29.11.60	13.9.62	Japanese Assoc.	Poly(vinyl alcohol)	Acrylates	Poly(vinyl alcohol) (I) graft copolymerization was carried out in two		623

				for Radiation Research on Polymers			ways: (a) I was irradiated while dipping in a solution of acrylate in an aqueous organic solvent; (b) I was irradiated and then heated in the above solution in the absence of air		
Japan	8,830(62)	7.12.60	20.7.62	Toyo Spinning Co.	Ethylene-propylene copolymers	Methyl methacrylate	Poly(ethylene-*co*-propylene) fibers are irradiated with γ-rays while immersed in a solution containing sodium poly(styrene sulfonate) (I), methyl methacrylate (II), methyl alcohol, and water and then heated at 80° for 7 hr. A copolymer of I and II is formed and is separated from the reaction mixture leaving the methyl methacrylate grafted fibers which are then washed and dried.	*CA*, 59, 12969	624
U. S.	3,137,674	9.12.60	16.6.64	W. R. Grace	Poly(ethylene)	Vinyl monomers, e.g., methyl acrylate, vinyl acetate, *N*-vinyl-2-pyrrolidone, 2-vinylpyridine, ethyl methacrylate, or ethyl acrylate	Graft copolymers having improved dyeability and increased elongation useful as wire coatings or heat-shrink films are prepared by mutual irradiation of poly(ethylene) and a di- or trialkyl compound followed by heating in the presence of a vinyl monomer	*CA*, 61, 5873	625
Brit.	940,139	22.12.60	23.10.63	B. X. Plastics	Vinyl halide polymers, e.g., poly(vinyl chloride)	Alkyl compounds and a synthetic rubber, e.g., chlorinated poly(ethylene)	Poly(vinyl chloride), an organotin stabilizer, stearic acid, dicumyl peroxide, a mixture of poly(vinyl chloride) and chlorinated poly(ethylene) are fused on a two roll-mill with roll temperatures of 120 and 150°C. The mixture is then worked for 5 min after gelling then pressed at 160° for 20 min.	*CA*, 60, 3170	626

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
Brit.	957,753	U. S. Appl. 23.12.60		American Cyanamid	Poly(ethylene) or poly(propylene)	Vinyl monomers selected from bis (2-chloroethyl) vinyl phosphonate, vinyl phosphonic acid, poly(vinyl benzyl sulfonic acid) and the alkali metal salts thereof	Claims an adhesionable, moldable, extrudable vinyl modified poly(ethylene) or poly(propylene) polymer, the vinyl group being grafted onto the poly(ethylene) or poly(propylene), the unmodified polymer being increased in weight from 0.1 to 20%. Also claims the preparation of a moldable, extrudable, adhesionable, vinyl-modified polyolefin, by irradiation and reacting poly(ethylene) or poly(propylene) with a vinyl monomer as specified, said monomer being present in an amount equal to between 0.5 parts to 20.0 parts by wt based on one part of the unmodified polymer. Also claims a process for bonding metal surfaces together which comprises inserting between heated metal surfaces a modified polyolefin as claimed	627
Fr.	1,307,490	U. S. Appl. 23.12.60		American Cyanamid	Equivalent to Brit. 957,753		See above	628
U. S.	3,192,178	29.12.60		Basdekis, C. H., Prill, E. J., and Walker, G. E.	Butadiene-styrene copolymer	A mixture of 65–90% styrene and 35–10% acrylonitrile	Claims polymeric blends of a resinous styrene-acrylonitrile copolymer, a graft copolymer prepared by polymerizing a mixture of styrene and acrylonitrile in the presence of a rubbery styrene copolymer and 1–6%, based on the weight of the blend of di-(hydroxy ethyl) sulfone	629

USSR	148,234	3.1.61	21.6.62	Rogovin, Z. A.	Cellulose	Vinyl monomers	The method of preparation of the copolymers by introducing into cellulose an amino group, which is then converted into a diazo group and which acts as initiator during grafting is modified by introduction of an aromatic amino group into the cellulose molecule by esterfication or alkylation; this method prevents formation of a homopolymer. The polymerization is carried out in presence of Fe^{2+}	*CA*, 58, 3558	630
U. S.	3,185,659	3.1.61	25.5.65	Esso Research and Engineering	Conjugated diolefin, e.g., poly(butadiene)	Monofunctional crosslinking monomer, e.g., styrene	Claims a method of preparing polydiolefin graft copolymers comprising adding a solution of peroxide catalyst in styrene to an oily liquid polymer of a conjugated diolefin in toluene. The mixture is then maintained at 115°C for 20 min and then cooled before adding divinylbenzene followed by more peroxide. Finally toluene is stripped from the resultant solution to obtain the product containing 40–60% nonvolatile material suitable for use in laminating		631
Belg.	612,235	U. S. Appl. 3.1.61		Esso Research and Engineering	Equivalent to U. S. 3,185,659		See above		632
Brit.	985,755	U. S. Appl. 3.1.61	10.3.65	Esso Research and Engineering	Equivalent to U. S. 3,185,659		See above		633

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	988,516	U. S. Appl. 13.1.61	7.4.65	American Machine and Foundry	Poly(ethylene)	Styrene	An easily substituted monomer, such as styrene, is grafted onto a more chemically stable backbone, such as poly(ethylene), by ionizing radiation, UV light or chemical means. Polar groups of opposite change such as SO_3H or NH_2 groups, are then introduced into the polymeric material	*CA*, 63, 4482	634
Japan	1,238(63)	18.1.61	19.2.63	Nisslin Cotton Spinning Co.	Poly(propylene)	Styrene	Addition of a reducing agent such as PhNHCOMe, acetylsalicylic acid, or $PhNH_2$ during the grafting of styrene to β- or γ-preirradiated poly(propylene), prevented the formation of homo polymer	*CA*, 59, 7676	635
Brit.	941,689	Swiss Appl. 23.1.61		Herberlein, J.	Cellulose	Acrylamide, an acrylate, a methacrylate, styrene, vinyl acetate, vinylidene chloride	Cellulose is first treated with a sensitizer and then subjected to ionizing radiation, the activated material being thereafter reacted with a graftable chemical substance		636
U. S.	3,106,482	23.1.61	8.10.63	Dow	Certain *N*-vinyl heterocyclic compounds	Acrylate and methacrylate monoesters of polyglycols	An antistatic agent for poly(acrylonitrile) fibers is prepared by graft copolymerising a mixture of monomeric acrylate and methacrylate monoesters of polyglycols onto certain *N*-vinyl heterocyclic compounds. This antistatic agent is incorporated in acrylonitrile fibers in an amount of 1–20% followed by conversion of the free acid form of the ternary polymer into an alkali metal salt	*CA*, 60, 3158	637

Japan	7,900(63)	27.1.61	3.6.63	Japan Radio-active High Polymer Research Foundation	Cellulose	Styrene	Viscose rayon stable is soaked in aqueous H_2O_2 irradiated with β-rays then soaked in an aqueous solution containing styrene, MeOH, and Fe_2SO_4 and heated at 50° for 4 hr	*CA*, 59, 8923	638
Japan	7,878(63)	28.1.61	3.6.63	Japan Radio active High Polymer Research Foundation	Cellulose	Styrene	Cellulose (cotton) immersed in a solution of styrene in acetone and irradiated with γ-rays *in vacuo*	*CA*, 59, 8939	639
Brit.	938,766	U. S. Appl. 30.1.61		W. R. Grace and Co.	Poly(ethylene)	Monomer which swells polythene	Poly(ethylene) film, swollen with monomer is immersed in a solution of a free radical generating compound at the melting point of the poly(ethylene) and cured in the absence of air. The grafting process improves clarity		640
Japan	18,387(62)	3.2.61	28.11.62	Toyo Spinning Co.	Proteins	Acrylonitrile	The protein of milk, yeast, corn, or soybeans is dissolved in a dilute alkali adjusted by acid at the pH of the isoelectric zone, acrylonitrile added and the mixture polymerized	*CA*, 59, 7721	641
Japan	9431(63)	9.2.61	17.6.63	Toyo Spinning Co.	Proteins	Acrylonitrile	Soybean protein in $ZnCl_2$ solution is added to a solution of acrylonitrile, $NaClO_3$ and $NaHSO_3$ and stirred for 2 hr at 3°C.	*CA*, 59, 8928	642

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Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Fr.	1,320,229	Japan Appl. 9.2.61		Toyo Spinning Co.	Equivalent to Japan 9,431(63)		See above		643
Belg.	625,479	Germ. Appl. 10.2.61	14.3.63	Rohm and Haas	SBR latex	Styrene, acrylonitrile methyl methacrylate or acrylic acid, amides, etc.	Said monomer mixture is polymerized in the presence of an SBR latex. These new graft copolymers have a high impact strength, a good form stability to heat and a high transparency	*CA*, 59, 4149	644
Fr.	1,294,752	U. S. Appl. 13.2.61		Dow	Acrylonitrile polymer or copolymer in aquagel state	*N*-vinyl heterocyclic monomer	Said polymer in the aquagel state is impregnated with a *N*-vinyl heterocyclic monomer and the product is exposed to high energy radiation and then treated in such a way that irreversible drying does not take place. The grafted polymer has improved dyeability		645
Fr.	1,288,829	14.2.61	30.3.62	Campagnie de Saint Gobain	Poly(vinyl chloride)	Vinyl chloride	An improvement in the radiochemical grafting onto PVC comprises maintaining during the irradiation, a temperature sufficiently low so that the monomer to be grafted cannot polymerize	*CA*, 57, 15372	646
Belg.	613,991	Germ. Appl. 16.2.61	16.8.62	Badische Anilin and Soda-Fabrik	Poly(formaldehyde)	Polyamides, polyamide esters, polyureas, polythioureas, polyurethanes, polyolefins, derived	Homogeneous graft copolymers are formed by heating poly(formaldehyde) at 100–210° with a radical producing catalyst and other thermoplastic materials	*CA*, 58, 2520	647

						from C_{2-6} hydrocarbons and vinyl derivatives			
Brit.	993,434	Germ. Appl. 16.2.61	26.5.65	Badische Anilin and Soda-Fabrik	Equivalent to Belg. 613,991		See above		648
U. S.	3,061,531 divided out of U. S. 3,012,001	17.2.61		United States Rubber Co.	Vinyl chloride polymer	Monomeric ester of an unsaturated dicarboxylic acid, together with a monomeric alcohol and styrene or its derivatives	The monomeric components together with the vinyl chloride polymer in specified proportions are irradiated in the solid state to form a graft mixture		649
U. S.	3,141,862	1.3.61	21.7.64	Esso Research and Engineering	Polyolefins, e.g., poly(ethylene,) poly(propylene), or poly(-1-butene)	Polar monomer, e.g., 4-vinylpyrridone, acrylonitrile, or vinyl chloride	Improved graft copolymers of polyolefins are claimed by the use of a boron alkyl, such as boron trihexyl, and oxygen or air followed by contacting the heated polymer with a polar monomer. Temperatures around 100° are suitable	*CA*, 61, 9636	650
Czech.	106,405	13.3.61	15.2.63	J. Pavlinec et al.	Poly(propylene)	Vinyl monomers and dicarboxylic acids or anhydrides	Poly(propylene) is oxidized by air or O_2 and the reactive sites thus obtained are grafted with a mixture of a vinylic monomer and an unsaturated dicarboxylic acid or its anhydride. The graft copolymer is then hydrolyzed with alkali	*CA*, 60, 10663	651

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Czech.	106,425	13.3.61	15.2.63	J.Pavlinec et al.	Poly(propylene)	Methyl methacrylate	Poly(propylene) is oxidized by air or O_2 and the active sites so formed are grafted with methyl methacrylate	*CA*, 60, 10863	652
Czech.	108,656	13.3.61	15.2.63	J. Pavlinec et al.	Poly(propylene)	Acrylonitrile	Modification with acrylonitrile via peroxide groups previously produced in the poly(propylene) by oxidization and subsequent partial hydrolysis of the grafted chains increases substantially the properties of poly(propylene)	*CA*, 60, 10863	653
U. S.	3,148,020	13.3.61	8.9.64	Du Pont	Polyolefins	Ethylenically substituted monomers	Graft copolymers are prepared by irradiating the organic polymer substrate with ionizing radiation prior to or during contact of the substrate with a mixture of SO_2 and the selected olefin	*CA*, 61, 16311	654
Brit.	963,771	U. S. Appl. 23.3.61	15.7.64	W. R. Grace	Poly(ethylene), poly(propylene), poly(vinyl chloride), poly(lower alkyl) acrylate or methacrylate, poly(vinylpyrrolidone) or poly(acrylonitrile)	Acrylonitrile, 2-vinylpyridine, N-vinyl-2-pyrrolidone, acrylic acid, vinyl acetate, methyl or ethyl acrylate, methyl or ethyl methacrylate or 2-ethyl hexyl acrylate	Claims a method of producing grafted vinyl polymers which comprises incorporating a free radical producing agent, having a $t \leqslant t\frac{1}{2}$ of the free radicals it produces, in a vinyl polymer substrate under vacuum or in an inert atmosphere, heating the polymer for a time sufficient to activate the agent but insufficient materially to diminish the concentration of the free radicals produced, bringing the activated polymer into contact with an ethylenically unsaturated graftable monomer and main-		655

							taining the polymer and monomer in contact at a temperature sufficient to induce diffusion of the monomer into the substrate polymer. The free radical producing agent may be lauroyl peroxide. A benzene dispersion or solution of the substrate polymer, example in benzene, is preferably used. The examples relate to the grafting of poly(ethylene) with acrylonitrile. Graft copolymers free from homopolymer are produced		
U. S.	3,130,177	24.3.61	21.4.64	Borg-Warner	Poly(butadiene)	Mixture of styrene and acrylonitrile	The thermoplasticity of polycarbonates is increased by blending them with graft copolymers prepared by polymerising styrene and acrylonitrile monomers in the presence of butadiene	*CA*, 61, 13485	656
Brit.	991,422	U. S. Appl. 24.3.61	5.5.65	Borg-Warner	Equivalent to U. S. 3,130,177		See above		657
Belg.	615,768	Germ. Appl. 29.3.61		Hoechst	Polydienes	α-Olefins	The graft copolymers may be effected at 0–60° with the polydiene dissolved in aromatic and/or aliphatic hydrocarbons. Mixed organometallic catalysts of the Ziegler type are used as initiators		658
U. S.	3,162,697	10.4.61		Phillips	Poly(propylene)	Mixture of alkyl acrylate monomers, e.g., methyl and butyl acrylates	A high surface area form of poly(propylene) is brought into contact with a mixture of alkyl acrylate monomers which are then polymerized with the aid of a peroxide or other catalyst		659

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	960,192	U. S. Appl. 20.4.61		U. S. Atomic Energy Commission	Cotton textile material	Acrylonitrile (Process claim)	Claims a method of uniformly coating a polymeric substrate material containing active H atoms which comprises irradiating said material in contact with an oxygen-free gas carrier containing water vapor and a vaporized polymerizable vinyl or vinylidene monomer with ionising radiation of sufficient energy to induce the formation of free radicals on said substrate, continuing to irradiate said substrate-vapor mixture until a uniform polymerized layer of desired thickness of said monomer has formed on the surface of said substrate, removing the resultant coated material from said gas and said radiation source and then separating the coated material from unadherent homopolymer. As an example, the coating of a textile material with poly(vinyl acetate) is described		660
Brit.	963,437	24.4.61	8.7.64	Imperial Chemical Industries	Polysiloxane	Oxyalkylenes	A polysiloxane containing Si bonded H is treated with an alcohol $[H(OC_nH_{2n})_q]_rR$ or a mixture of alcohols comprising at least one polyhydric alcohol or at least one alcohol of the previous formula, in such proportions that the resulting siloxane-oxyalkylene copolymer contains	*CA*, 61, 8479	661

							on the average at least one oxylakylene unit to three Si atoms		
Japan	4,494(63)	27.4.61	24.4.63	Kureha Chemical Industry Co.	Methyl methacrylate copolymers	Vinyl chloride	Azodiisobutyronitrile is used to polymerise MeM in the presence of tertiary Bu permethacrylate. To the polymer dissolved in MeOH is added copper naphthenate, ascorbic acid, and vinyl chloride and the mixture heated at 40° for 17 hr	*CA*, 59, 6356	662
U. S.	3,177,268	1.5.61		Borg-Warner	Diene rubber, at least the majority of the latex particles having a size of less than 1,000 Å	A mixture of acrylonitrile and styrene	Claims a molding composition comprising a blend of poly(methyl methacrylate) and a graft copolymer of a diene rubber and a mixture of a vinyl cyanide and a vinyl aromatic hydrocarbon. The resulting blend, which is suitable for injection molding or extrusion has an improved melt index compared with either of the components resins		663
Brit.	991,315	U. S. Appl. 1.5.61	5.5.65	Borg-Warner	Equivalent to U. S. 3,177,268		See above		664
Belg.	617,057	U. S. Appl. 3.5.61	15.5.62	American Viscose Corp.	Cellulose crystallites	Acrylic derivatives especially acrylonitrile	The crystallites are treated with a reducing agent to convert the potential aldehyde groups at the end of each chain to hydroxyls. Reaction with acrylic derivatives is done at pH < 5 in the presence of a Ce salt	*CA*, 58, 1602	665
Brit.	1,000,082	U. S. Appl. 3.5.61	4.8.65	FMC Corp.	Equivalent to Belg. 617,057		See above	*CA*, 63, 16550	666

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Germ.	1,132,724	3.5.61	5.7.62	Chemische Werke Hüls	Polymers containing hydroxyl groups	Vinyl monomers	Grafting of vinyl monomers onto polymers containing OH groups is achieved with $HClO_4$	*CA*, 58, 5854	667
Brit.	942,971	Germ. Appl. 3.5.61		Chemische Werke Hüls	Equivalent to Germ. 1,132,724		See above		668
Belg.	617,230	Germ. Appl. 5.5.61		Farbenfabriken Bayer	Polyoxyalkylene or polyalkylene glycol derivatives	Vinyl monomers	Vinyl monomers are polymerized in emulsion with free radical catalysts in the presence of said polymer, one or more nonionic emulsifier and optionally ionic emulsifiers in specified proportions		669
Belg.	617,260	Fr. Appl. 6.5.61	5.11.62	Pneumatiques et Caoutchouc Manufacture Kleber-Colombes	Poly(tetrafluoroethylene)	Styrene, acrylic acid	PTFE is treated with styrene vapor for 1 hr at 170° then placed in a stream of oxygen containing ozone for 30 min and then in a chamber containing acrylic acid for 1 hr at 100°. Grafted product has improved adhesion, dyeability and inking characteristics	*CA*, 58, 10366	670
Fr.	1,300,770	8.5.61		Dow	Cellulose	Vinyl monomers	Cellulose substrate in form of films, fibers or fabrics is impregnated with an aqueous solution of a monomer and exposed to high energy ionizing radiation		671
U. S.	3,131,163	9.5.61	28.4.61	Van Kohorn Constructors	Copolymer of styrene and itaconic anhydride	Acrylonitrile	Solution polymerization of acrylonitrile in a $MeCONMe_2$ solution of a copolymer of styrene and itaconic anhydride yields colorless	*CA*, 61, 5841	672

							polymers having good dyeability and heat stability		
USSR	146,033 addition to USSR 131,084	11.5.61	6.4.62	H. K. Moygova, V. V. Horshah, J. V. Ergorova	Natural wool		To obtain graft copolymers with better mechanical properties, natural wool is applied as the initial polymer for modification, and the preliminary heating is carried out at 110–120°C	*CA*, 57, 10049	673
Fr.	1,299,556	15.5.61	18.6.62	A. Hemeryck	Poly(vinylcarbazoles) styrene-butadiene copolymers, polyvinylidenes, poly(vinyl ketones), and amino plastics	Vinyl, alkyd, maleic and acrylate resins	Activated centers on the chain of the polymer are obtained by means of γ-radiation. A mixture of polymer solution and plasticizer is passed through a condenser producing free radicals that induce the polymer to link to the monomer or plasticizer	*CA*, 58, 2516	674
U. S.	3,143,522	19.5.61	4.8.65	Firestone Tire and Rubber	Butadiene-styrene copolymers containing 100–60% butadiene and up to 40% styrene	Styrene	A high-impact styrene plastic consisting of styrene and butadiene, is produced by dissolving 2–25% of an elastomeric copolymer of butadiene and styrene, in 98–75% of styrene, then forming a suspension with 100 parts of this solution using 100–300 parts of water and 0.1–3.0 parts of poly(vinyl alcohol), and polymerizing the styrene at 35–135°C with 0.2 parts of phenylcyclohexane hydroperoxide as catalyst	*CA*, 61, 16285	675
Germ.	1,151,660	24.5.61		B.A.S.F.	Poly(styrene) or derivatives	Butadiene, isoprene, 2,3-dimethylbutadiene	Poly(styrene) is treated with metallic Na or K in ether and reacted with said monomer. The graft reaction takes place at −100° to +30°C in ether solution		676

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Fr.	1,335,508	5.6.61	28.8.63	S. A. Progil	Poly(vinyl chloride), poly(vinyl butyral)	α-Methyl styrene, low mol wt polymer	Polymers can be plasticized by graft polymerization at 50–100° with a monomer or low mol wt polymer. Thus poly(vinyl chloride) is mixed with butyl benzyl phthalate, epoxide resin, and diethylenetriamine, homogenized and cured for 8 hr at 100°C.	*CA*, **60**, 737	677
U. S.	3,134,746	9.6.61	26.5.64	Borg-Warner Corp.	Poly(butadiene)	Mixture of a vinyl cyanide and a vinyl aromatic hydrocarbon	Claims a blend of poly(caprolactam) and a graft copolymer of 10-60% by weight poly(butadiene) and 40–90% by weight of a mixture of an alkenyl cyanide and an alkenyl substituted mononuclear aromatic hydrocarbon with good tensile strength, elongation, hardness, and stability	*CA*, **61**, 7201	678
Brit.	990,194	U. S. Appl. 9.6.61	28.4.65	Borg-Warner Corp.	Equivalent to U. S. 3,134,746		See above		679
U. S.	3,162,695	26.6.61		Borg-Warner Corp.	Copolymer of butadiene and styrene	Mixture of methyl methacrylate and styrene	Claims a blend of polycarbonate [e.g., 2,2′(4,4′ dehydroxy-diphenyl)-propane] and a graft copolymer containing butadiene, styrene, and methyl methacrylate which has the desirable properties of the polycarbonate but with improved flow	*CA*, **62**, 10618	680
Brit.	992,503	U. S. Appl. 26.6.61	19.5.65	Borg-Warner Corp.	Equivalent to U. S. 3,162,695		See above		681

Ital.	652,608	27.6.61	15.2.63	Mazzucchelli Celluloide	Copolymer of butadiene-styrene	Styrene	Shock-resistant styrene butadiene copolymer graft copoylmers, which are useful for printing processes and have improved resistance to heat, cold, and atmospheric agents are prepared by hot-working a copolymer of styrene and non-stabilized polybutadiene (3–50%) before adding a phenolic antioxidant	*CA*, 63, 13501	682
Fr.	1,326,931	Germ. Appl. 28.6.61		Hoechst	Copolymers of ethylene with α-olefins or α-olefin copolymers	Acrylamide, and/or its *N*-substituted derivatives	Grafting by transfer initiated with free radical catalyst		683
Czech.	108,675	10.7.61	15.10.63	J. Pavlinec et al.	Poly(propylene)	Specified methacrylates	Graft copolymerization of poly (propylene) with $CH_2{=}CMeCO_2CH_2CH_2OH$ via peroxidic and hydroperoxidic functional groups	*CA*, 60, 10863	684
Brit.	951,128	21.7.61		Koppers Co.	Polymer or copolymer of butadiene, styrene, isoprene, chloroprene, methyl of higher alkyl acrylate or methacrylate or vinyl acetate	Olefinic monomer, preferably styrene	Polymer is mechanically worked in the viscoelastic state in the presence of oxygen to form degraded polymer chains containing active functional groups. A solution containing said degraded polymer chains and one or more monomer is then polymerized		685
Brit.	1,017,533	25.7.61 16.11.61	19.1.66	B. X. Plastics	Poly(vinyl chloride) or vinyl chloride copolymers	Mixtures of butadiene and acrylonitrile or chloroprene and ethyl acrylate or butadiene and methyl methacrylate	Claims a polymer blend comprising a chlorinated PVC and a graft copolymer obtained by graft polymerizing one or more monomers, at least one of which contains two conjugated carbon-carbon bonds, onto PVC or a vinyl chloride copolymer		686

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	3,170,964	31.7.61	23.2.65	Borg-Warner Corp.	Diene rubber latex	A mixture of acrylonitrile and styrene	Claims polymeric blends comprising poly(methyl methacrylate), a graft copolymer prepared by polymerizing acrylonitrile and styrene with a small-particle size (500–700 Å) polymerised diene rubber, and a graft copolymer prepared by polymerizing acrylonitrile and styrene with a large particle size (1600 Å) diene rubber	*CA*, 62, 11978	687
Brit.	991,316	U. S. Appl. 31.7.61	5.5.65	Borg-Warner Corp.	Equivalent to U. S. 3,170,964		See above		688
Fr.	1,333,966	U. S. Appl. 2.8.61		American Cyanamid	Poly(propylene)	Chloromethylstyrene	Poly(propylene) fibers irradiated in vacuo with ionizing radiation and then treated with chloromethylstyrene monomer		689
USSR	148,908 addition to USSR 136,557	7.8.61	20.7.62	L. M. Shuter et al.	Albuminous substances	Acrylates	Grafted film materials are obtained by polymerization of albuminous substances with acrylates. To impart freezing resistance to the films, a mixture of Me and Bu acrylates is treated with the albuminous component followed by treatment according to method described in main patent	*CA*, 58, 2552	690
Japan	22,490(63)	17.8.61	23.10.63	Japan Rayon Co.	Rayon	Styrene, acrylonitrile	Rayon yarn is soaked in an acrylonitrile, styrene, Na lauryl sulfate emulsion, $K_2S_2O_8$ in $AgNO_3$ solution added and shaken *in vacuo* at 30°	*CA*, 60, 1885	691

Fr.	1,331,159	Germ. Appl. 23.8.61		Chemische Werke Hüls	Poly(tridecyl acrylate)	Vinyl chloride	Suspension or emulsion polymerization of vinyl chloride in the presence of catalysts soluble in water or in the monomers, together with a polymerized emulsion of tridecyl acrylate		692
Brit.	1,009,109	Germ. Appl. 23.8.61	3.11.65	Chemische Werke Hüls	Equivalent to Fr. 1,331,159		See above		693
Japan	90(64)	30.8.61	11.1.64	Toyo Spinning Co.	Cyanoethylated or carboxymethylated protein	Vinyl monomer especially acrylonitrile	The protein is dissolved in poly(acrylonitrile) with a vinyl monomer and subjected to graft polymerization	*CA*, 60, 13380	694
Isralei	15,962	30.8.61	25.10.62	Zilkhi, A. B. Feit, and A. Bar-Nun	Natural polyhydroxyl compounds and derivatives and synthetic polyhydroxy polymers	Vinyl monomers	The polyhydroxy backbone is first converted into alkoxy derivative and then treated with the monomer in an appropriate solvent (liq NH_3, THF etc). Under these conditions the alkoxy derivative serves as anionic catalyst for the monomer polymerization	*CA*, 58, 5803	695
Fr.	1,333,311	Brit. Appl. 7.9.61		B. X. Plastics	Poly(vinyl chloride) or a copolymer of vinyl chloride	Monomers containing an ethylenic double bond	Crosslinking said polymer with one or more monomers containing an ethylenic double bond, using ionising radiation or UV light, in the presence of a free radical polymerized sensitizer or initiator or two or more of these compounds		696
U. S.	3,130,076	29.9.61		American Cyanamid	(Process claim)		Claims a continuous process for grafting a vinyl monomer onto the cellulose chains of a paper web involving precautions against the encouragement of side reactions. The apparatus is described in detail		697

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Belg.	623,166	U. S. Appl. 3.10.61 23.2.62 22.6.62		Yardney Int. Corp.	Nonreducing polymer with hydrophobic and electrostatic properties, e.g., a polyamide	Ethylenic monomer, e. g., acrylic acid	The monomer is polymerized in the presence of a catalyst comprising a compound of a rare earth or actinide metal and in the presence of said polymer. The catalyst preferably contains cerium; and a polyacid derivative such a maleic anhydride may also be present		698
Japan	18,956(64)	10.10.61	4.9.64	Toyo Spinning Co.	Poly(vinyl chloride)	Acrylonitrile	Acrylonitrile is grafted onto PVC in a solvent, consisting of 70–80% Me_2SO_4 and 30–20% halogenated hydrocarbon or alkylbenzene, to give a homogeneous solution which can be used for spinning	*CA*, 62, 16436	699
Fr.	1,337,602	U. S. Appl. 25.10.61 26.10.61		W. R. Grace	Poly(ethylene)	Isocyanates	Graft copolymers are formed by reacting a hydroxylated poly(ethylene) at above its melting point with an isocyanate such as benzyl isocyanate, 2,4-toluene isocyanate or hexamethylene diisocyanate		700
Brit.	971,607	U. S. Appl. 25.10.61 26.10.61	30.9.64	W. R. Grace	Equivalent to Fr. 1,337,602		See above	*CA*, 62, 16480	701
Austrl.	23,536/62	Germ. Appl. 27.10.61 (24.10.62)		Farbwerke Hoechst	Polyethers, polyether acetals, and polyacetals	Trioxane	Claims a graft polymer of trioxane or a primary polymer selected from the group consisting of polyethers, polyether acetals and polyacetals		702

Brit.	965,851	U. S. Appl. 6.11.61	Monsanto	Butadiene or isoprene polymer or copolymer with, e.g., styrene, acrylonitrile, etc.	Mixture of 20–100% by weight of a monovinylidene aromatic compound, e.g., styrene, with up to 80% of acrylonitrile or methacrylonitrile	Claims a blend of a monovinylidene aromatic compound superstrate/diene rubber substrate graft copolymer with a rigid monovinylidene aromatic compound polymer having a narrow mol wt distribution such that there is a difference of not greater than 0.05 specific viscosity units between the specific viscosity of the highest mol wt 10% of the polymer and the highest mol wt 95% of the polymer	703
Brit.	961,797	U. S. Appl. 15.11.61	Monsanto	Copolymer of butadiene-styrene	Mixture of styrene and acrylonitrile	Claims a blend preferably comprising a styrene-acrylonitrile superstrate/butadiene-styrene rubber substrate graft copolymer containing 40–60 parts by weight of superstrate/100 parts by weight of substrate, a styrene-acrylonitrile copolymer, and a dual stabilizer system consisting of 2,6-di-*t*-butyl-*p*-cresol and tris (nonylphenyl)-phosphine in respective amounts of 0.1–1% and 1.4%, based on the weight of the graft copolymer substrate	704
Fr.	1,339,286	Brit. Appl. 16.11.61	B. X. Plastics	Poly(vinyl chloride) or a copolymer of vinyl chloride	Vinyl monomer	Patent refers to a blend comprising a chlorinated poly(vinyl chloride) or chlorinated copolymer of vinyl chloride and a graft copolymer obtained by grafting one or more monomers onto poly(vinyl chloride) or a copolymer of vinyl chloride	705

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Fr.	1,307,117	20.11.61	19.10.62	B. X. Plastics	Poly(vinyl chloride)	Diolefins, vinyl or acrylic derivatives	Claims transparent compositions of improved tensile and impact strength consisting of a graft copolymer of poly(vinyl chloride) with diolefins and (or) other vinyl or acrylic derivatives	*CA*, 58, 6999	706
Japan	3,718(65)	20.11.61	26.2.65	Japan Irradiation Polymerisation Research Association	Cellulose	Mixture of butadiene and styrene	Cellulose, butadiene and styrene are copolymerized in methanol under γ-irradiation to yield a graft copolymer	*CA*, 63, 7190	707
Brit.	962,028	U. S. Appl. 28.11.61	24.6.64	Rayonier Inc.	Fibrous cellulosic material	Vinyl or vinylidene compound, e.g., acrylic or methacrylic acid or their methyl esters, vinyl esters or nitriles	Claims a process of graft polymerizing fibrous cellulosic material while retaining the general physical structure or form of the untreated fibrous cellulosic material which comprises providing cellulosic material having reactive sites to which polymers become attached, grafting on the fibrous cellulosic material a vinyl or a vinylidene compound in an acid aqueous solution of a salt or complex of Mn (III) with a polyphosphate which is an initiator for the grafting. The products are useful as ion-exchangers		708
U. S.	3,183,056	28.11.61	11.5.65	W. R. Grace	(Process claim)		Claims a graft polymerization process in which a fibrous web of	*CA*, 63, 11862	709

							cellulose containing absorbed therein an aqueous solution of a graft polymerization peroxygen initiator is immersed in a body of liquid ethylenically, unsaturated, monomeric material having a boiling point above 120°C, and is soon thereafter contacted with the vapor of another monomeric material at atmospheric pressure, the temperature of the vapor being between 50° and 100°C		
Belg.	625,434	Netherlands Appl. 30.11.61		Shell	Polyolefins	Olefinically unsaturated hydrocarbons	Polymerization of olefinically unsaturated hydrocarbons in contact with already polymerized particles kept in a fluidized state by means of a gas stream is carried out using one or more trihalides of Ti and/or V and one or more aluminium alkyls		710
Japan	11,390(65)	7.12.61	7.6.65	Japan Rayon Co.		(Process claim)	Graft copolymers are prepared by pretreatment of reducing polymers with silver and persulfate ions in aqueous media and subsequent copolymerization with gaseous vinyl monomers	*CA*, 63, 16501	711
Japan	18,980(64)	8.12.61	4.9.64	Dainippon Spinning Co.		(Process claim)	Graft polymerization of vinyl compounds onto natural or regenerated high polymers is effectively carried out by using ionizing radiation in the presence of a metal cation, such as Sn^{2+} Sn^{4+}, Ti^{3+}, Pb^{2+}, Co^{2+}, Mn^{2+} and Cr^{2+}	*CA*, 63, 725	712

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Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
U. S.	3,144,420	18.12.61	11.8.64	Koppers	Poly(styrene)	Butadiene-styrene	A conjugated diolefin rubber is dissolved in styrene and the solution is mixed with a solution of poly(styrene) in styrene. The mixture is homogenised and an initiator added. The product, which is believed to consist of poly(styrene) chains with styrene-elastomer side chains, is derived preferably from 72–87% styrene, 5–20% poly(styrene), and 5–8% rubber	*CA*, 61, 10841	713
U. S.	3,167,598	18.12.61	26.1.65	B. X. Plastics	Poly(vinyl chloride)	A mixture of a conjugated diolefin such as butadiene and a monomer such as ethyl acrylate, methyl methacrylate, styrene, or acrylonitrile	Claims blends of a chlorinated polymer or copolymer of vinyl chloride and a graft copolymer prepared by copolymerizing said monomer mixture onto PVC. The product is easily processed and has a high impact strength	*CA*, 62, 10548	714
USSR	157,108	22.12.61	25.9.63	Z. Rogovin and R. M. Livshits	Polymers with reducing properties	Water soluble vinyl monomers	Graft copolymers are obtained by polymerization of water soluble vinyl monomers in the presence of a polymer having groups with reducing properties (CHO, NH_2, CO) and oxidizing agents especially V(V) compounds	*CA*, 60, 5663	715
Brit.	965,627	Germ. Appl. 29.12.61		B.A.S.F.	Polymers of vinyl chloride, a vinyl ester, a vinyl	Azo and/or anthroquinone dye bearing a poly-	Claims macromolecular organic substances colored by graft polymerization with a dye bearing a		716

					ether, an acrylic ester, a methacrylic ester, an acrylic amide, a methacrylic amide, acrylonitrile, methacrylonitrile, styrene, or vinylpyrrolidone	merisable olefinically unsaturated group, e.g., 1-amino-4-acryloylaminoanthraquinone-2-carboxylic acid isobutyl ester	polymerizable olefinically unsaturated group and, if desired, other monomers which are colorless. Grafting is by transfer in an emulsion system		
Fr.	1,347,976	Germ. Appl. 29.12.61	3.1.64	B.A.S.F.	Equivalent to Brit. 965,627		See above	*CA*, 62, 4156	717
Japan	15,658(65)	30.12.61	21.7.65	Dainippon Spinning Co.	(Process claim)		Graft copolymers can be prepared under mild conditions by irradiating a polymeric substrate with a dose $> 5 \times 10^4$r under air or oxygen followed by contact with monomers which are reactive to free radicals, in the presence of Ti^{3+} salts	*CA*, 63, 18371	718
Japan	18,970(64)	12.1.62	4.9.64	Toyo Rayon	Nylon 6	Acrylic acid, methacrylic acid, or vinyl acetate	Nylon 6 fiber heated with $(NH_4)_2S_2O_8$ aqueous solution (0.05 m/l) at 60°C for 10 min is exposed to an acrylic acid-water vapor mixture at 80°C for 10 min to give 17% grafting of acrylic acid. The grafted material is then dipped into an aqueous nickel acetate solution (0.1 m/l) at 50°C for 10 min to give a nonmelting polyamide fiber with high resistance to heat and light. The use of cobalt salts instead of nickel salts is also recommended	*CA*, 63, 731	719

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Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Fr.	1,354,773	16.1.62		Kleber-Colombes	Chlorine-containing polymers, e.g., PVC, PTFCE, chlorinated poly(ethylene)	"Vinylidene" monomers, e.g., styrene, methyl methacrylate, or acrylic acid	Polymerizing a vinylidene monomer that is polymerizable by a radical mechanism, comprising heating a chlorine-containing polymer in the presence of one or more monomers which swell said polymer, such heat being effected at between room temperature and the decomposition temperature of said monomer		720
Brit.	998,979	Fr. Appl. 15.1.62 16.1.62	21.7.65	Kleber-Colombes	Poly(ethylene), poly(propylene), PVC, poly(acrylonitrile), or a vinyl chloride-vinylidene chloride copolymer	Vinylidene monomer, e.g., acrylic and methacrylic acids, methyl methacrylate, ethyl acrylate, acrylonitrile, and methacrylonitrile	Claims a polymerization process comprising the step of heating a crystalline homopolymer or copolymer in the solid state and free from residual polymerization catalyst at a temperature between the melting point of the polymer and 20°C below said melting point, in the presence of a vapor of one or more vinylidene monomers polymerizable in accordance with a radical type mechanism		721
Japan	3719(65)	20.1.62	26.2.65	Japanese Irradiation Polymerisation Research Association	Cellulose	Mixture of styrene and acrylonitrile	Cellulose, styrene, and acrylonitrile and mixed with methanol and irradiated with Co^{60}-γ radiation. When the components of the polymerization solution are styrene 5–55%, acrylonitrile 5–55%, and methanol 25-70%, the degree of graft copolymerization is the highest	*CA*, **63**, 7171	722

Japan	9970(65)	20.1.62	21.5.65	Japanese Irradiation Polymerisation Research Association	Poly(vinyl alcohol)	Radical-polymerizable monomers	Pretreatment of poly(vinyl alcohol) by impregnating with a solution of peroxides, such as H_2O_2 or $K_2S_2O_8$, followed by irradiation in air or by processing in the reverse order and subsequent copolymerization at 30–80°C with radical polymerisable monomers in mixed organic-aqueous solutions containing 10^{-2} to 10^{-5} mole. Fe^{2+} salts/l. in the presence of air gave graft copolymers	*CA*, 63, 18339	723
Belg.	627,414	Fr. Appl. 22.1.62		Kleber-Colombes	Poly(vinyl chloride)	Vinylidene monomer and a copolymerizable ethylenic anhydride	PVC foam is prepared by heating a mixture of PVC, polyisocyanate, heat decomposable gas generating agent, vinylidene monomer and a copolymerizable ethylenic anhydride in a mold under pressure and in the presence of a saturated halogenated hydrocarbon. The copolymer is chain grafted onto the PVC		724
Brit.	965,866	Germ. Appl. 27.1.62		Farbwerke Hoechst	Poly(*N*-vinylpyrrolidone)	Vinyl esters, e.g., vinyl acetate	Claims a process for the manufacture of graft copolymers of vinyl esters, wherein one or more of the esters is polymerised in admixture with poly(*N*-vinylpyrrolidone) under the action of a free radical forming polymerization initiator and/or UV radiation. Also claims graft copolymers from poly(*N*-vinylpyrrolidone) and one or more vinyl esters		725

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Belg.	628,348	Germ. appl. 14.2.62	29.5.63	Farbenfabriken Bayer	Poly(butadiene)	An acrylate, e.g., butyl acrylate and $CH_2=CRCONR^1CH_2OR^2$(I) or $CH_2=CRCONR^1CH_2R_4R_5$(II) where $R_1=Me$ $R_2=H$ $R=Me$, $CHCl_2$ $(CH_2)_2CN$ CH_2CO_2Na, $(CH_2)OSO_3Na$ or $(CH_2CH_2O)_{10}H$ and R_4 =morpholine, Et or Bu, R_5 =morpholine Et or $(CH_2)_2OSO_3Na$	Stable aqueous dispersions of grafted copolymers which crosslink spontaneously to yield elastic and strong films, resistant to aging, light, and heat, are prepared by emulsifying a diene (3–30%), an acrylate (95.4–60%), and 0.5–10% of either I or II by the addition of an emulsifying agent. The acrylate can be replaced up to 50% by I or II	*CA*, **60**, 16077	726
Belg.	629,046	Germ. Appl. 28.2.62	28.8.63	Hoechst	Copolymers of vinyl chloride	Butadiene, isoprene or conjugated dienes of higher mol wt	Vinyl chloride is copolymerized with a suitable monomer in aqueous emulsion to 70–85% conversion, an elastomer latex is then added and the polymerization continued. The graft reaction may be accelerated with UV or hard particle rays		727
Japan	7072(65)	28.2.62	7.4.65	Karashiki Rayon	Poly(oxymethylene)	Vinyl monomer, e.g., methyl methacrylate	Treatment of poly(oxymethylene) with a radical polymerization initiator and a vinyl compound is described	*CA*, **63**, 3140	728
Belg.	629,203	U. S. Appl.	13.2.63	Atlas Chemical	Water dispersible polymer, e.g.,	Vinyl monomers	The polymeric substrate is irradiated in air at ⩽ 70°. It is then contac-	*CA*, **60**, 13397	729

		5.3.62		Industries	starch, casein, etc.		ted with an aqueous dispersion of the monomer. The aqueous phase contains a catalyst, e.g., Fe(II), Ti(III), or Hg(I) salts, to initiate free radical formation from the peroxides or hydroperoxides		
Austri.	27,939/63	U. S. Appl. 5.3.62		Atlas Chemical Industries	Equivalent to Belg. 629,203		See above		730
South Africa	63/838	U. S. Appl 5.3.62		Atlas Chemical Industries	Equivalent to Belg. 629,203		See above		731
Hung.	151,336	8.3.62	25.4.64	Muanyagipari Kutato Intezet	Poly(propylene)	Polymerizable unsaturated compounds	Treatment of heated poly(propylene) during or after fiber formation with hot oxygen, especially in the case of simultaneous stretching, results in the formation of peroxide and hydroperoxide groups attached to the fibers. In the absence of oxygen, these groups initiate the grafting of unsaturated compounds capable of polymerization	*CA*, 61, 5840	732
Germ.	1,174,991	21.3.62	30.7.64	Farbwerke Hoechst	Poly(vinyl-pyrrolidene)	Vinyl acetate	Vinyl acetate and poly(vinylpyrrolidene) in methanol are polymerized in 4 hr under reflux with azodiisobutyronitrile to yield a graft copolymer of said constituents	*CA*, 61, 8439	733
Belg.	630,088	U. S. Appl 27.3.62	21.10.63	Du Pont	Ethylene homo- or copolymers	Polar vinylidene monomers especially acrylonitrile or acrylamide	The polymeric substrate is firstly crosslinked with for example ar-(methacryloyloxy) acetophenone and then exposed to UV radiation in the presence of the monomer	*CA*, 60. 16072	734

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
Brit.	981,049	U. S. Appl. 27.3.62 28.9.62	20.1.65	Du Pont	Equivalent to Belg. 630,088		See above	735
U. S.	3,111,370	5.4.62		Toyo Kagaku	Poly(vinyl alcohol)	Vinyl chloride	Vinyl chloride is grafted to poly(vinyl alcohol) in an emulsion system. The graft copolymer is mixed with further poly(vinyl alcohol) and spun into fibers	736
Brit.	981,584	Fr. Appl. 7.4.62	27.1.65	Kleber-Colombes	Poly(propylene)	Acrylic acid	Claims a process for dyeing poly(propylene) fibers consisting of ozonizing the fibers in the presence of a phenolic compound, a thiophenolic compound, or an aromatic amine compound, and grafting onto these ozonized fibers polymerizable monomers having affinity for dyes	737
U. S.	3,196,124	16.4.62		Inter-chemical Corp.	Benzoguanamine-formaldehyde resins	A mixture of monomers including 5–30% of 2-hydroxymethyl-5-norbornene, 60–95% of an acrylic type ester and up to 35% of methacrylic acid	Claims a graft copolymer comprising the addition polymer of a mixture of said monomers and benzoguanamine formaldehyde resins. Also claims a heat curable white ink containing the composition	738
Fr.	Additional Patent 82,070 addition	18.4.62		Centre Nationale de la Researche	Poly(styrene), poly(methyl methacrylate), and polyamides	Methyl methacrylate, isoprene, ethylene oxide, styrene, vinyl-	The patent particularly refers to rigid-polymerized compounds in the mesomorphous state formed from a straight chain or graft	739

	to Fr. 1,295,524			Scientifique		2-pyridine	polymer in which the molecular chains are directly crosslinked by a crosslinking agent		
Fr.	1,367,487	Germ. Appl. 21.4.62	24.7.64	Farbenfabriken Bayer	Polyesters, e.g., poly(ethylene glycol adipate), poly(diethylene glycol adipate), poly(triethylene glycol adipate), or polytriethylene glycol azelate)	Vinyl acetate, vinyl chloride or mixtures thereof	Claims film-forming graft copolymers prepared by polymerizing vinyl monomers in the presence of polyesters having mol wt 900	*CA*, 62, 6645	740
Brit.	987,353	Germ. Appl. 21.4.62	24.3.65	Farbenfabriken Bayer	Equivalent to Fr. 1,367,487		See above		741
USSR	158,063	27.4.62	18.10.63	V. V. Korshak, K. K. Mozgova and T. M. Babchinitser	Poly(tetrafluoroethylene) and poly(trifluorochloroethylene	Vinyl monomers	Films of poly(tetrafluoroethylene) and poly(trifluorochloroethylene) are immersed in monomer and heated in an inert gas at 60–130°C for 4–8 hr	*CA*, 60, 10889	742
Isralei	17,225	2.5.62	24.10.63	Nehemia Salomon	Poly(2-ethyl hexyl acrylate)	Methyl methacrylate	Grafting is by transfer, initiated with $K_2S_2O_8$ or 30% H_2O_2 and sodium formaldehyde sulfoxylate	*CA*, 60, 9437	743
Fr.	1,342,435	U. S. Appl. 2.5.62		Rayonier Inc.	Cellulose	Methyl methacrylate	Hydrophobic graft copolymers of cellulose and methyl methacrylate are produced by heating a hydrofilic graft copolymer of cellulose and methyl methacrylate containing 1–30% PMMA at above 105°C for 10–180 min		744

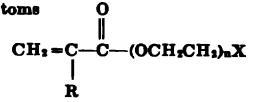
(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Belg.	630,843	U. S. Appl. 3.5.62		United States Rubber	The rubbery component may be a natural rubber or a homopolymer of butadiene or isoprene or their copolymers with up to 30% of a copolymerisable olefinically unsaturated monomer. The resin may be a homo- or copolymer of styrene, chlorostyrene, methylstyrene, lower alkyl (meth)acrylate, vinyl chloride, vinyl naphthalate, vinyl acetate, vinylidene chloride, methacrylonitrile, methacrylic acid, maleic anhydride, or a lower alkyl maleate or formarate		Patents refers to blend, comprising a mixture of hard nonelastic resin, a graft copolymer compatible with the resin of a resin-forming monomer with a rubbery component, and a nonvolatile oil miscible with the rubber component and practically immiscible with the resin		745
Brit.	1,001,953	U. S. Appl. 17.5.62	18.8.65	American Cyanamid	Poly(butadiene), poly(isoprene), poly(methyl methacrylate-*co*-butadiene), poly(acrylonitrile-*co*-butadiene) or a rubbery alkyl acrylate copolymer	Butadiene, isoprene, or mixtures of methyl methacrylate and butadiene	Claims a thermoplastic molding composition comprising a physical blend of a copolymer of a methacrylic acid ester and acrylonitrile or substituted acrylonitrile and a graft copolymer of a "rubbery" monomer onto a "rubbery" polymer backbone		746
Belg.	632,249	U. S. Appl. 17.5.62	18.11.63	American Cyanamid	Equivalent to Brit. 1,001,953		See above	*CA*, 61, 12167	747
Germ.	1,161,423	23.5.62	16.1.64	Farbenfabriken Bayer	Polyvinyl esters	Monocarboxylic acids or acrylates	The graft copolymerization is initiated with a free radical catalyst and takes place in the presence of polyacetals prepared from formaldehyde and di- or triethylene glycol	*CA*, 60, 13342	748

Belg.	631,408	U. S. Appl 23.5.62		United States Rubber Co.	Poly(butadiene) rubber	Mixture of styrene and acrylonitrile	Patent refers to a blend comprising a mixture of an aliphatic diamine and a graft copolymer of styrene-acrylonitrile on poly(butadiene) rubber		749
Brit.	968,578	U. S. Appl. 23.5.62	2.9.64	United States Rubber	Equivalent to Belg. 631,408		See above		750
Brit.	982,918	Germ. Appl. 23.5.62	10.2.65	Farben-fabriken Bayer	Polyacetal, e.g., polyacetal obtained from formaldehyde and monoethylene glycol diethylene or triethylene glycol with mol wt between 500 and 5,000	Vinyl ester, e.g., vinyl acetate or ethyl acrylate	Claims a process for the production of graft polymers, wherein at least one vinyl or vinylidene compound is polymerized in the presence of a polyacetal		751
Belg.	618,194	28.5.62	28.11.62	Solvay-Cie	Poly(vinyl chloride) or poly(vinylidene chloride)	Vinyl monomers especially 2-ethyl hexyl acrylate	Poly(vinyl chloride) is expoxidized by treatment with an alkali followed by treatment with a peroxide solution such as acetic acid in ethyl acetate containing sodium acetate. The expoxidized poly(vinyl chloride) is then heated *in vacuo* with the monomer	*CA*, 58, 10326	752
Brit.	967,288	Belg. Appl. 28.5.62		Solvay-Cie	Equivalent to Belg. 618,194		See above		753
Fr.	1,367,558	U. S. Appl. 4.6.62		W. R. Grace	Poly(ethylene)	Maleic acid diesters	Claims compositions prepared from a polycarbonate, polycarboxamide, or a poly(oxymethylene) and a grafted copolymer containing poly(ethylene) and 0.5–12 wt % maleic acid diester	*CA*, 62, 5402	754

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Japan	9964(65)	7.6.62	21.5.65	Furukawa Electric	(Process claim)		Claims the irradiation of polymers by ionizing radiation in the presence of oxidizing vapors and subsequent treatment with a mixed vapor of vinyl monomers and amines or DMF to yield graft copolymers with smaller amounts of vinyl homopolymers	*CA*, 63, 16550	755
Belg.	633,903	Germ. Appl. 22.6.62	20.12.63	B.A.S.F.	Copolymer of butadiene and an ester of an unsaturated carboxylic acid, e.g., *n*-butyl acrylate or ethyl hexyl acrylate	Styrene or its mixture with acrylonitrile	Styrene or its mixture with acrylonitrile is polymerized in the presence of said preformed component in stated proportion. The polymerization may be carried out in the presence of solvents dissolving all the reactants	*CA*, 61, 4549	756
Brit.	979,652	Germ. Appl. 22.6.62	6.1.65	B.A.S.F.	Equivalent to Belg. 633,903		See above		757
Brit.	1,017,861	U. S. Appl. 22.6.62	19.1.66	Yardney International Corp.	Polyamides, poly(propylene), or poly(ethylene terephthalate)	Acrylic acid	Claims a process for producing a graft polymer without the use of a polymeric organic reducing agent comprises the step of treating a nonreducing polymeric material with a polymerizable monomeric material having a reactive group —CH =C < in the presence of a graft polymerization catalyst having the formula $Ma\ (A)m.Ha$ A wherein M is a metal selected from the group consisting of rare earth and actinium elements, A is an acid anion, m is the valence of		758

							the metal M and is the integer 3 or 4, and a is the valence of the anion A		
Fr.	1,360,643	U. S. Appl. 22.6.62		Dow	Polymer of a mono-olefin containing 2–8 C atoms	Monomer of general formula  $CH_2=\underset{R}{\underset{\mid}{C}}-\overset{O}{\overset{\|}{C}}-(OCH_2CH_2)_nX$ in which R is H or CH_3, X is halogen, OH, alkoxy, acrylate, methacrylate, or 1–4 C alkyl and n is 2–200	Claims the graft copolymerization of one or several of the monomers of the general formula indicated, onto a substrate consisting of a polymer of a mono-olefin containing 2–8 C atoms		759
U. S.	3,222,323	27.6.62	7.12.65	Dow	Alkenyl aromatic polymers, e.g., poly(styrene)	Anhydrides of unsaturated debasic acids, e.g., maleic anhydride	Alkenyl aromatic polymers are acrylated in the presence of $AlCl_3$ by the anhydride of an unsaturated dibasic acid, to give products in which only one of the acid radicals is acylated to the polymer molecule. The second acid radical is available for conversion to derivatives and the unsaturated group is available for crosslinking	*CA*, 64, 5261	760
Belg.	634,284	29.6.62		Japanese Association for Radiation Research on Polymers	Polyesters, e.g., poly(ethylene terephthalate)	Vinyl monomers	The polyester in the form of fiber, film or powder is grafted with the vinyl monomer in the presence of a swelling agent. The grafting is achieved by the preirradiation technique		761

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Fr.	1,334,518	29.6.62	9.8.63	Societe Nationale des Petroles D'Aquitaine	Poly(butadiene), or poly(isoprene)	Styrene	The polymer is dissolved in styrene at 110°C, dodecyl mercaptan, an anionic soap, $CaCl_2$, and Na_3PO_4 are added and the mixture agitated in the presence of *t* butyl perbenzoate at 100°C.		762
Fr.	1,351,387	3.7.62	7.2.64	Produits Chimiques Pechiney-Saint-Gobain	Poly(vinyl chloride) polymers or copolymers containing at least 50% poly(vinyl chloride)	Mixtures of diene and acrylic ester monomers	A mixture containing a diene and an acrylic ester monomer, antioxidant, stabilizer, and plasticizer, etc. is graft copolymerized to a vinyl chloride polymer by a free radical catalyst in emulsion at 30–80°	*CA*, 61, 2014	763
Fr.	Additional Patent 82,090 to Fr. 1,276,804	6.7.62		Pechiney-Compagnie de Produits Chimiques et Electrometallurgiques	Polymer or copolymer of vinyl monomers	Diene or ethylenic monomers	A polymer latex in aqueous emulsion is prepared in presence of a water soluble peroxide with the addition of a mineral reducing salt; the grafting monomer is added and the mixture heated at 10–90°C for 5–20 hr	*CA*, 60, 13342	764
Belg.	634,545 Addition to Belg. 609,158	Fr. Appl. 6.7.62		Produits Chimiques Pechiney-Saint-Gobain	Equivalent to Fr. Addn. 82,090 (1,276,804)		See above		765

Belg.	634,955	U. S. Appl. 16.7.62	15.1.64	Dow	Poly(vinyl chloride)	Styrene, methyl methacrylate	Styrene or methacrylate is added to PVC and the mixture homogenized. After the application of heat and pressure the sample is irradated with high energy radiation to initiate grafting	*CA*, 62, 1799	766
Belg.	635,415	Brit. Appl. 25.7.62	18.11.63	B. X. Plastics	Halogenated polymer, e.g., PVC	A mixture of a mono-vinyl monomer, e.g., acrylonitrile, acrylic esters, styrene or methacrylates a conjugated diolefin, e.g., butadiene, isoprene, chlorobutadiene or 2,3-dimethyl butadiene and a small amount of a divinyl monomer, e.g., divinyl benzene, ethylene glycol dimethacrylate, divinyl ether or divinyl sulfide	Claims high impact strength polymer blends of a copolymer of vinyl chloride and vinyl acetate and a graft copolymer of PVC	*CA*, 61, 12157	767
Fr.	1,395,558	U. S. Appl. 2.8.62 7.1.63		Yardney International Corp.	Cellulose, polyamides, polyalkyllenes, polyesters or polyacrylics	Methacrylic acid, vinylpyrrolidone, vinylidene chloride, styrene	Graft copolymers are produced by reacting a preformed polymer in the presence of a metal in colloidal form, e.g., Ag, Au, Cu, Ni, or Pt as activator and a graft copolymerization catalyst, e.g., a peroxide or persulfate		768

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Japan	12,185(65)	13.8.62	16.6.65	Japan Carbide Industries	Poly(vinyl pyrrolidone)	Vinyl chloride	Claims the polymerization of vinyl chloride in the presence of 0.1–20% poly(vinylpyrrolidone) with radical sources including inorganic peroxides and azobisnitriles to give graft copolymers of improved heat stability, mechanical strength and dyeability	*CA*, 63, 18368	769
USSR	170,675	18.8.62	23.4.65		Polymeric peresters	Vinyl compounds	Vinyl compounds are copolymerized with a monomeric or polymeric perester, then another vinyl compound is grafted onto the first peroxide copolymer at the position of the peroxide group	*CA*, 63, 11728	770
Japan	21,272(65)	18.8.62	21.9.65	Japan Telegram and Telephone Corp.	Polyolefins, e.g., poly(propylene)	Butadiene	Irradiation of polyolefins in the presence of butadiene vapor is described	*CA*, 64, 2236	771
Belg.	636,450	Ital. Appl. 23.8.62		Sicedison	Rubbery copolymer	A mixture of vinyl and/or vinylidene monomers such as styrene and acrylonitrile	Claims impact resistant polymer compositions incorporating a graft copolymer of a mixture of vinyl monomers onto a rubbery copolymer containing preferably at least 85% but not more than 95% of a conjugated diene hydrocarbon		772
Brit.	972,229	U. S. Appl. 31.8.62	7.10.64	United States Rubber	Rubbery copolymer comprising an ethylene-propy-	Styrene, chlorostyrene, methyl styrene, or acry-	Claims impact-resistant compositions incorporating a styrene/ethylene-propylene rubber graft copolymer.		773

				lene copolymer, ethylene-propylene-dicyclopentadiene terpolymer or ethylene-propylene hexadiene-1,4-terpolymer	lic acid esters	The compositions may be used for sheets for vacuum forming, for coating, unsupported films, or for expanding with a blowing agent	
Belg.	635,024	U. S. Appl. 31.8.62	United States Rubber	Equivalent to Brit. 972,229		See above	774
Belg.	636,977	Germ. Apl. 4.9.62	Farbenfabriken Bayer	Copolymers of ethylene and vinyl esters of which the ester group contain lower alkyl or aryl radicals especially vinyl acetate	Vinyl chloride	The copolymer and free radical catalyst is dissolved in vinyl chloride, the solution dispersed in aqueous medium with dispersion additives and then polymerized	775
Belg.	636,997	U. S. Appl. 4.9.62	Rohm and Haas	Polymers containing an oil-solubilizing group prepared from at least one ethylenically unsaturated polymerizable ester chosen from alkyl esters of methacrylic acid, itaconic acid and/or fumaric acid, a vinylic ester of an alkanoic acid or mixtures thereof	Itaconic or maleic anhydride	Claims oil soluble graft copolymers prepared by first polymerizing said monomer under the influence of a free radical initiator until 50–90% conversion adding itaconic or maleic anhydride and continuing the polymerization	776

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	983,817	4.9.62	17.2.65	R. H. Cole and Co.	Methacrylate polymer or copolymer, e.g., poly(methyl methacrylate)	A methacrylate ester and an unsaturated diester, e.g., di-2-ethyl hexyl maleate or di-2-ethyl hexyl fumarate	Describes a process for the production of synthetic resins in which a methacrylate polymer or copolymer is copolymerised with a methacrylate ester an unsaturated diester. Also claims a surgical or similar device to be employed in contact with the skin comprising a synthetic resin as claimed		777
Brit.	997,674	Japan Appl. 6.9.62	7.7.65	Toyo Kagaku Col.	Poly(vinyl alcohol)	Vinyl chloride	Claims a spinning dope comprising an emulsion containing a graft copolymer of vinyl chloride and vinyl alcohol, and a free polyvinyl alcohol, said emulsion having a viscosity of less than 200 cp at a temperature of 30°C and a particle size of less than 500 Å		778
Japan	20,514(64)	8.9.62	19.9.64	Showa Denko	Chlorinated poly(ethylene)	A mixture of acrylonitrile and methyl methacrylate	The polymerization of acrylonitrile and methyl methacrylate in the presence of chlorinated poly(ethylene) results in a graft copolymer mixture with good transparency and nonflammability	*CA*, 63, 1954	779
Japan	16,155(65)	10.9.62	26.7.65	Research Institute for Production Development	Cellulose	Methyl methacrylate	The graft copolymerization of cellulose with vinyl monomers in the presence of salts of Group VIII metals, can be accelerated by an ultrasonic treatment	*CA*, 63, 18456	780
Brit.	1,015,304	U. S. Appl. 17.9.62	31.12.65	B. F. Goodrich	Poly(butadiene) rubber	A mixture of styrene and acrylonitrile	Claims a chlorinated poly(vinyl chloride) composition having improved process ability which in-		781

							corporates from 3 to 50 parts by weight of a graft copolymer of styrene and acrylonitrile onto a poly(butadiene) rubber backbone		
Austral.	35,260/63	U. S. Appl. 17.9.62		B. F. Goodrich	Equivalent to Brit. 1,015,304		See above		782
Fr.	1,369,703	Japan Appl. 18.9.62	14.8.64	Shin Nippon Chisso Hiryo	Olefinic (co) polymers with tertiary carbon atoms	Vinyl compounds	Graft copolymers are prepared from olefinic polymers with tertiary carbon atoms, by hydroperoxidation of the polyolefin while irradiating with UV light in the presence of a light sensitizer and oxygen. The hydroperoxidized polyolefin is then brought into contact with a liquid vinyl compound. The graft copolymerization is carried out in the presence of a solvent, water, and as reducing agent, a low valency compound of a polyvalent metal		783
Fr. addn.	84,634 (addn to Fr. 1,343,784)	Germ. Appl. 3.10.62		Deutsche Gold und Silber Scheideanstalt	In process of copolymerizing unsaturated polyesters with graftable unsaturated monomers, at above 30°C according to the parent patent, an improvement is claimed characterized in that the reaction medium contains at least one organic compound containing a second enolizable or enolized group and at least one aromatic radical on the carbon or nitrogen atom adjacent to the first carbonyl group of the opposite side, optionally also using materials known to be used in copolymerization reactions such as peroxides, imines, inhibitors, etc.				784
Belg.	638,208	Germ. Appl. 5.10.62	3.2.64	Farbenfabriken Bayer	Conjugated diolefin polymer	A mixture of 50–90% styrene and 50–10% acrylonitrile	Claims a mineral-oil grafted copolymer mixture containing 5–60% of graft of said composition 10–92% of a thermoplastic copolymer of styrene and acrylonitrile and 3–30% of mineral-oil. The product can be molded and has good low temperature mechanical properties	*CA*, 62, 9333	785

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Belg.	638,209	Germ. Appl. 5.10.62	3.2.64	Farbenfabriken Bayer	Poly(butadiene)	Mixture of styrene and acrylonitrile	Thermoplastic molding compositions of good shock and rupture resistance are prepared by polymerizing styrene and acrylonitrile mixtures (50:50 to 90:10) in the presence of poly(butadiene) latexes	*CA*, 62, 9316	786
Belg.	638,556	Germ. Appl. 11.10.62		Hoechst	Compounds containing ethylene polyglycol groups		Aqueous dispersions of ethylene polymers grafted on compounds containing polyglycol groups are produced by polymerising ethylene, optionally in the presence of other polymerizable ethylenic compounds in aqueous alkaline reaction medium under pressure of 250–280 atmospheres at 50–160°C in the presence of water soluble persulfates as free radical polymerization initiators and 1.5–20%, based on the water used, of oxyethylated fatty alcohols or acids		787
Brit.	994,924	U. S. Appl. 16.10.62	10.6.65	American Cyanamid	Natural or synthetic rubber, e.g., poly(butadiene)	Monomer possessing ethylenic unsaturation e.g. methyl methacrylate, styrene, or acrylonitrile	Claims transparent thermoplastic moulding compositions characterized by their high impact strength, transparency rigidity and weatherability containing from 5–50 parts by wt of a natural or synthetic rubber having grafted thereon at least one monomer possessing ethylenic unsaturation		788

Belg.	636,312	U. S. Appl. 31.10.62	16.12.63	United States Rubber			Graft copolymers of acrylonitrile, butadiene, and styrene can be stabilized against changes in color and thermal degradation by Group II metal sulfides. The stabilizers are used in addition to conventional stabilizers		789
Fr.	1,372,908	Germ. Appl. 3.11.62	18.9.64	Chemische Werke Hüls	Chlorinated ethylene-propylene copolymers	Vinyl chloride or a mixture of vinyl chloride and acrylic acid	Vinyl chloride is polymerized in the presence of a chlorinated ethylene-propylene copolymer to give products with good shock-resistant properties	*CA*, 62, 10619	790
Belg.	636,696	U. S. 7.11.62		United States Rubber	Poly(butadiene) rubber	Acrylonitrile, styrene, α-methyl styrene, acrylic acid, or methacrylic acid	The butadiene rubber, preferably crosslinked, is intensively mixed in the presence of a free radical polymerization initiator with at least one of the said monomers		791
Japan	15,821(65)	10.11.62	22.7.65	Toyo Spinning	Proteins, e.g., soybean	Acrylonitrile	Graft copolymerization of proteins and acrylonitrile is carried out in > 35% aqueous thiocyanates containing 5–30% lower aliphatic alcohols. The product is spun to give silklike fibers	*CA*, 64, 2235	792
Japan	15,822(65)	10.11.62	22.7.65	Toyo Spinning	Proteins, e.g., soybean	Acrylonitrile	Copolymerizations similar to those of Japan 15,821(65) were carried out in > 10% aqueous urea	*CA*, 64, 2236	793

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Germ.	1,171,157	15.11.62	27.5.64	Hoechst	Polymers of open chain, tertiary *N*-vinyl-amides	Vinyl esters optionally mixed with other monomers	Polymerizing a vinyl ester in the presence of polymers of open chain tertiary *N*-vinyl-amides optionally in the presence of organic solvents, under known conditions. Preferred amide polymer is poly(*N*-vinyl-*N*-methyl acetamide) and the ratio of vinyl ester to polymer may be 1:99 to 99:1. The polymers obtained are suitable for use as varnishes, textile auxiliaries, emulsifiers, adhesives, etc.		794
Belg.	640,039	Germ. Appl. 15.11.62		Hoechst	Equivalent to Germ. 1,171,157		See above		795
Fr.	1,363,890	19.11.62	19.6.64	Societe d' Electro-Chimie, d'Electro Metallurgie et des Acieries Electriques d'Ugine	Poly(butadiene) or butadiene-styrene copolymers	A mixture of methyl methacrylate, styrene, and acrylonitrile	Thermoplastic compositions of good impact resistance and heat distortion temperature are made from PVC or vinyl copolymers containing ⩾ 50% vinyl chloride, and poly(butadiene) or butadiene-styrene copolymers which have been grafted with methyl methacrylate, styrene, and acrylonitrile		796
Belg.	639,890	Fr. Appl. 19.11.62		Societe d'Ugine	Equivalent to Fr. 1,363,890		See above		797
Fr.	1,347,881	22.11.62	3.1.64	Kleber-Colombes	Ethylene propylene rubber (EPR)	Styrene	The rubber is dissolved in CCl_4 and ozonized air passed through the	*CA*, 60, 16088	798

							solution. The ozonized rubber is precipitated with alcohol, dried, and sealed in an ampule with styrene and DMA. The ampule is left standing at room temperature for 48 hr to complete the grafting reaction		
Fr.	1,348,550	28.11.62	10.1.64	Kleber-Colombes	Polyether, or polyester containing —OH groups	Vinyl monomers, e.g., acrylamide acrylic acid, and maleic anhydride	A stream of ozone-containing oxygen is bubbled through the polyether, the monomer is dispersed in the ozonized polyether, and the mixture heated 1 hr in vacuo at 130° to form a graft copolymer. The product is then treated with a polyisocyanate to give sponges with good hydrophilic properties	*CA*, 60, 14704	799
USSR	159,657	8.12.62	28.12.63	Livshits, R. M., and Z. A. Rogovin	Polymers containing groups with reducing properties such as OH, CHO, and CO	Vinyl monomers	Vinyl monomers are polymerized in the presence of polymers containing groups with reducing properties and an oxidizing agent. To obtain an end product free of homopolymer a Mn(III) compound is used as the oxidizing agent	*CA*, 61, 741	800
Germ.	1,182,830	22.12.62	3.12.64	Farbenfabriken Bayer	Copolymer of a (meth)acrylate with up to 30% w/w poly(isopropyl α-methyl styrene)	A monomer containing the terminal group $CH_2=C<$	Claims shock resistant thermoplastic graft copolymers having good mechanical properties prepared by polymerizing a vinyl monomer in an emulsion of said copolymer		801
Belg.	641,598	Germ. Appl. 22.12.62		Farbenfabriken Bayer	Equivalent to Germ. 1,182,830		See above	*CA*, 62, 6639	802
Fr.	1,378,500	Ger. Appl. Appl. 22.12.62		Farbenfabriken Bayer	Equivalent to Germ. 1,182,830		See above		803

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Belg.	641,599	Germ. Appl. 22.12.62	16.4.64	Farbenfabriken Bayer	Copolymer of a (meth)acrylate with up to 30% w/w poly(isopropyl α-methyl styrene)	Acrylic acid ester with 1–10 C atoms and in which 50% of the acrylic ester can be replaced by another olefinic unsaturated component containing terminal vinyl groups and copolymerisable with the acrylic ester, e.g., hydroxymethyl ethers	Claims graft copolymers for copolymers for coating, impregnating, sealing, or laminating prepared by polymerizing said monomer in an emulsion of a copolymer of a methylate and isopropyl α-methyl styrene	*CA*, 63, 734	804
Fr.	1,385,684	Germ. Appl. 22.12.62		Farbenfabriken Bayer	Equivalent to Belg. 641,599		See above		805
Belg.	626,518	24.12.62	15.4.63	B.A.S.F.	Poly(propylene)	Ethylenic monomers, e.g., vinylpyrrolidone	Poly(propylene) is hydroperoxidized with oxygen and heated with ethylenic monomers containing polar groups in solution at 100° to form graft copolymers	*CA*, 61, 5874	806
Belg.	641,894	U. S. Apl. 26.12.62		Dow	A butadiene polymer containing a major proportion of chemically combined 1,4-butadiene, especially 32–55% *cis*-1,4-structure	Monovinyl aromatic compounds or acrylonitrile	Polymerization of at least two monomers having different degrees of reactivity is carried out in the presence of a rubbery polymer or a mixture of rubbery polymers. A solution of the rubbery polymer in at least part of the monomers is heated to a temperature known to		807

							cause grafting and polymerization to form a prepolymer, while subjecting the solution to sufficient shearing; stirring to keep the grafted rubbery polymer in suspension in the prepolymer as particles or droplets not larger than 10 μ until the prepolymer contains 20–50% solids; any remaining monomer is added and polymerization is carried out by heating and stirring the partially polymerized soluton while it is mixed with an inert medium containing a dispersing agent and in which it is suspended as droplets		
Brit.	1,013,393	Japan Appl. 27.12.62	15.12.65	Nitto Chemical Industry	Poly(butadiene) latex	Styrene or a mixture of styrene and acrylonitrile monomers	Claims a method for producing a styrene containing graft polymer comprising subjecting to polymerizing conditions a mixture of styrene and acrylonitrile monomers (containing at least 50% styrene) in the presence of a poly(butadiene) latex. The polymer has a superior processability and yields shaped products of excellent surface glaze and high impact strength		808
Belg.	638,939	U. S. Appl. 27.12.62	17.2.64	United States Rubber	Poly-l-olefin, e.g., poly(ethylene), or poly(propylene)	Styrene or styrene and acrylonitrile	Compositions which can be rapidly extruded to give brilliant and smooth objects consists of a mixture of a graft copolymer of said components and a rubber compatible with the grafted copolymer	*CA*, 62, 12000	809

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Belg.	641,883	Brit. Appl. 28.12.62	29.6.64	Imperial Chemical Industries	Poly(lauryl methacrylate)	Vinyl chloride	Artificial leather and nonwoven fabrics are produced by impregnating fibres with a dispersion of an elastomeric binder such as PVC, a vinyl chloride copolymer, a polyacrylate, or a butadiene copolymer, and a graft copolymer stabiliser of said composition in a volatile organic liquid containing a plasticizer. The mixture is squeezed and heated	*CA*, 63, 11827	810
Fr.	1,358,415	Japan Appl. 8.1.63	17.4.64	Nitto Chemical Industry and Nitto Physico-Chemical Research Institute	Poly(butadiene) emulsions	Monomer mixture containing at least 5–100% wt styrene	Claims poly(butadiene) emulsions having particles 0.2–0.6 μ in diameter and gel content of at least 75% upon which is grafted styrene. The grafted product was readily extruded and had a glossy surface	*CA*, 61, 7192	811
Fr.	1,358,757	Japan Appl. 16.1.63	15.1.65	Kanegafuchi Spinning Co.	Proteins, e.g., casein	Ethylenic monomer	Proteins are treated with a nitrile compound (containing an epoxy group, a halogenated group, or ethylenic unsaturation) to give protein derivatives which are then graft polymerised with an ethylenic monomer. Viscose and an emulsion of the graft copolymer are spun to give elastic fibres with good flexion strength	*CA*, 63, 13472	812
Fr.	1,378,024	24.1.63	13.11.64	Pneumatiques, Caoutchouc Manu-	Crystallizing poly(acrylonitrile)	Vinyl monomers, e.g., acrylic acid	Vinyl monomers are polymerized at 120–40°C in the presence of crystallizing poly(acrylonitrile) to give products with good dye affinity	*CA*, 62, 6638	813

				facture et Plastiques. Kleber-Colombes					
Belg.	642,979	U. S. Appl. 28.1.63	18.5.64	Cosden Oil and Chemical	Poly(butadiene) of narrow mol wt distribution	Styrene	A poly(butadiene) having a narrow mol wt distribution such that $^3/_4$ of its weight lies within 2 units of specific viscosity is incorporated in poly(styrene) either by mixing the two preformed polymers or by graft polymerizing styrene directly into the poly(butadiene)	*CA*, 63, 4478	814
Belg.	643,168	Germ. Appl. 31.1.63	18.5.64	Dynamite-Nobel	Copolymers of ethylene and vinyl acetate or ethylene and acrylic acid	Vinyl chloride	Shock-resistant graft copolymers are obtained by reacting 5–40% vinyl chloride with said copolymers	*CA*, 63, 5863	815
USSR	166,094	2.2.63	10.11.64		Cellulose	Methyl methacrylate	Claims a process for the modification of grafted copolymers in which copolymers of cellulose and poly(methyl methacrylate) are treated with an alcoholic alkaline NH_2OH solution to give polymeric complexons	*CA*, 62, 6591	816
Neth. Appln	288,606	6.2.63	10.3.65	Shell Internationale Research Maatschappij	Polymers containing styrene substituents, e.g., copolymer of isobutylene with divinylbenzene	Vinyl monomer containing a heterecylic ring with a nitrile group, e.g., 2-vinylpyridine or 4-vinylpyridine	Graft copolymers suitable as soil-dispersing additives in lubricating oils are prepared by anionic polymerization of a said vinyl monomer onto polymers containing styrene substituents	*CA*, 63, 2833	817
Brit.	1,001,331	Neth. Appl. 6.2.63	18.8.65	Shell Internationale Research Mattschappij	Equivalent to Neth. Appl. 288,606		See above		818

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
USSR	173,949	11.2.62	6.8.65	State Scientific Research Institute of Plastics	Fluorine containing polymers	Vinyl monomers	The method of obtaining graft polymers by grafting vinyl monomers to fluorine containing polymers in the presence of an initiator is modified by using cerium-ammonium nitrate as the indicator	*CA*, 64, 2189	819
Belg.	643,626	Germ. Appl. 11.2.63	11.8.64	Farbenfabriken Bayer	Ethylene-vinyl acetate copolymers	Vinyl chloride	Claims a process for crosslinking graft copolymers of vinyl chloride on ethylene-vinyl ester copolymers by heating at 40–180° in the presence of a free radical forming substance or by exposure to ionising radiation at room temperature	*CA*, 63, 3141	820
Japan	9861(65)	14.2.63	20.5.65	Hani Chemical Industry Co.	Alkyd resins	Acrylic acid and/ or methacrylic acid	Water-soluble alkyd resin graft copolymers are prepared by polymerizing 2–80 parts of resin with 1–10 parts acrylic or methacrylic acids and 97–10 parts of their esters and subsequent treatment with amines or ammonia	*CA*, 63, 16576	821
Irish Appln	152/1964	19.2.63		International Synthetic Rubber	Polydienes such as poly(butadiene), poly(isoprene), or copolymers of a diene and monomers such as styrene or acrylonitrile	Unsaturated organic oils, e.g., vegetable oil, cod oil, or sperm oil	Claims graft copolymers of polydienes with unsaturated organic oils. The process of production comprises heating a mixture of the base polymer and said oil to between 50°C and 350°C. For grafting at relatively low temperatures a free radical forming catalyst may be used		822
Neth. Appln	64,01515	Brit. Appl.	20.8.64	International	Equivalent to Irish appln. 152/1964		See above		823

		19.2.63		Synthetic Rubber					
Brit.	996,090	25.2.63	23.6.65	International Synthetic Rubber	Unsaturated homopolymer or copolymer of butadiene	Unsaturated organic oil	Claims an epoxy graft copolymer of an unsaturated organic oil with said polymer. Also claims a process for the preparation of an epoxy graft copolymer which comprises epoxidizing a graft copolymer of an unsaturated organic oil and unsaturated polymer of butadiene	*CA*, 63, 7171	824
Fr.	1,393,595	Brit. Appl. 25.2.63		International Synthetic Rubber	Equivalent to Brit. 996,090		See above		825
Belg.	643,940	Fr. Appl. 7.3.63		Societe d'Ugine	Butadiene or copolymers of butadiene and styrene	Monomer composition comprising 35–49% methyl methacrylate, 60–35% styrene, and 5–15% acrylonitrile	Claims mixtures of 40–60 parts of poly(metyl methacrylate) or its copolymer with one or more (meth) acrylic esters, (meth)acrylonitrile and (α-methyl)styrene and 60–40 parts of a graft copolymer of butadiene and a mixture of monomers of said composition		826
Belg.	644,936	Brit. Appl. 15.3.63	9.9.64	Imperial Chemical Industries	Degraded natural rubber	Methyl methacrylate	Film-forming polymers are dispersed in organic liquids in which they are insoluble by using graft or block copolymers as the dispersion media. Portions of these copolymers are compatible with the film former and the other parts are solvated by the organic solvent. Thus high mol wt poly(methyl methacrylate) was dispersed in kerosine using the above mentioned graft copolymer	*CA*, 63, 11872	827

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	1,002,456	26.3.63	25.10.65	Monsanto Chemicals	Copolymers of a C_{2-4} alkene and a diester of an unsaturated dicarboxylic acid	Cyclic or acyclic diolefins, such as butadienes, cycloalkadienes, butadienyl alkyl ethers, and bis-esters of unsaturated carboxylic acids	Cyclic or acyclic diolefins are graft polymerized in an emulsion system to said copolymers (I) to give graft polymers containing 60–70 wt % I.	*CA*, 63, 15107	828
USSR	173,946	2.4.63	6.8.65		Cellulose	Ethylenic monomers	The method of obtaining graft copolymers of cellulose by means of radical copolymerization using the decomposition products of hydroperoxide groups as initiators is modified by introducing aldehyde groups into the cellulose	*CA*, 64, 2275	829
Belg.	646,284	U. S. Appl. 8.4.63	8.10.64	Scott Paper Co.	Cellulose	Ethylenic unsaturated monomers	Graft copolymers are prepared by the free radical polymerization of ethylenically unsaturated monomers in the presence of a thiocarbonic acid or metal thiocarbonic derivative of a cellulose material	*CA*, 63, 11862	830
Belg.	646,285	U. S. Appl. 8.4.63	8.10.64	Scott Paper Co.	Cellulose	Ethylenically unsaturated monomers	Ethylenically unsaturated monomers are added to the ferric salts of the adducts of cellulose with alkylene episulfides to give graft copolymers	*CA*, 63, 11798	831
Fr.	1,393,730	U. S. Appl. 8.4.63		Du Pont	"Ionomers" may be prepared from graft copolymers		Ionic hydrocarbon polymers are prepared by copolymerizing α-olefins with an ethylenically unsaturated monocarboxylic acid. Distributed throughout the structure is a metal ion having an ionized valency of		832

							1,2, or 3. The α-olefin may be a copolymer of ethylene, methacrylic acid, and a third monomer, vinyl acetate. The copolymer may be a graft copolymer		
Brit.	1,001,437	U. S. Appl. 10.4.63	18.8.65	B. F. Goodrich	Homopolymers of butadiene or copolymers of butadiene-acrylonitrile wherein butadiene is the major constituent	Mixture of monomers comprising 25–80% methyl methacrylate, 10–40% styrene, and 5–40% acrylonitrile	Claims a resinous, transparent, impact resistant graft copolymer composition comprising the interpolymerized product of from 65–90 part by weight of said monomer mixture and from 10–35 parts by wt of a poly(butadiene) rubber. Also claims a process for preparing such a graft copolymer in an aqueous emulsion medium		833
Belg.	646,258	U. S. Appl. 10.4.63	31.7.64	B. F. Goodrich	Equivalent to Brit. 1,001,437		See above	*CA*, 63, 11826	834
Fr.	1,395,993	U. S. Appl. 22.4.63		Dow	Polymers of ethylene or propylene	Acrylic or methacrylic acid	Compounding, at the softening temperature, a normally solid resinous polymer of ethylene or propylene previously irradiated with high energy causing radiation in an oxygen containing atmosphere the polymer being in the form of fine particles, and the operation being carried out whilst contacting the polymer softened by heat with acrylic or methacrylic acid		835
Belg.	641,842	U. S. Appl. 7.5.63	16.4.64	De Bell and Richardson Inc.	Elastomeric latices, e.g., polybutadiene copolymers	Ethylenic monomers	Ethylenic monomers are graft copolymerized with elastomeric latex, such as a butadiene copolymer, in aqueous suspension to give shockresistant products.	*CA*, 62, 14911	836

(*continued*)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Neth. Appln	64,05132	U. S. Appl. 10.5.63	11.11.64	Union-Carbide Corp.	Copolymers of butadiene and styrene	Mixtures of styrene and acrylonitrile	Claims styrene-acrylonitrile graft copolymer blends with butadiene-styrene copolymers of high impact strength prepared by a two stage continuous process in which the first stage polymerization is performed at a solids content $<40\%$, while the second stage is performed at a high solids content	*CA*, **62**, 13345	837
Neth. Appln	64,05932	U. S. Appl. 10.5.63		Union Carbide Corp.	Butadiene-styrene copolymers	Mixtures of styrene and acrylonitrile	Claims the process by which the blends described in the above patent (Neth. Appln. 64,05132) are prepared		838
Fr.	1,403,867	Brit. Appl. 15.5.63		Imperial Chemical Industries	(Process claim)		Claims dispersions of synthetic polymers, in which the links between the monomer or comonomers which form the polymeric chain include another atom other than carbon are produced by precipitation of the polymer in the form of particles dispersed in an organic liquid in the presence of a block or graft copolymer, in the organic liquid, containing a polymeric constituent which is dissolved by the organic liquid and another polymeric constituent with a different degree of polarity which is not dissolved by the organic liquid but is associated with the precipitated particles of the polymer		839
Belg.	648,686 (addn to	Germ. Appl.		Farbwerke Hoechst	Ter-polymers of ethylene, α-ole-	Acrylamide or *N*-alkyl substituted	Acrylamide or *N*-alkyl substituted derivatives thereof are grafted onto		840

	Belg. 619,525)	31.5.63			fines, dienes or trienes	acrylamides	ternary copolymers of ethylene in aqueous dispersion using formaldehydesodium bisulfite. The product is useful for upgrading paper		
Neth. Appln	64,06144 (addn to Neth. Appl. 280,106)	Germ. Appl. 31.5.63		Farbwerke Hoechst	Equivalent to Belg. 648,686		See above	*CA*, 63, 5853	841
USSR	173,404	17.6.63	21.7.65		Cellulose	Esters of acrylic or methacrylic acid, including glycidyl acrylate or methacrylate	Graft copolymers are prepared by free radical graft copolymerisation of cellulose with an ester of acrylic or methacrylic acid. Ion-exchange properties are imparted to the graft by treating with compounds that react with its α-oxide rings, e.g., aqueous solutions of 1° or 2° amines, $NaHSO_3$, or Na_2SO_3	*CA*, 64, 887	842
Neth. Appln	64,06384	Ital. Appl. 17.6.63	5.6.64	Montecatini	Amorphous polymers of mol wt 1,000–500,000 formed from olefins of formula $CH_2=CHR$ (where R is alkyl), from amorphous linear copolymers of these α-olefins and/or with ethylene, or amorphous linear terpolymers of these α-olefins with ethylene and a diene hydrocarbon	Vinyl chloride	Claims graft copolymers of vinyl chloride onto said amorphous polymers the amount of amorphous polymer being from 5–25%.		843

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Fr.	1,369,447	29.6.63	14.8.64	Centre National de la Recherche Scientifique	Poly(vinyl chloride)	Mixtures of styrene and acrylonitrile	Poly(vinyl chloride) which is swelled with mixtures containing styrene and 95–8% acrylonitrile, is subjected to ionizing radiation *in vacuo* to give copolymers with improved physical properties	*CA*, 61, 16252	844
Brit.	1,007,884	Fr. Appl. 29.6.63	22.10.65	Centre National de la Recherche Scientifique	Equivalent to Fr. 1,369,447		See above		845
Fr.	1,405,589	Germ. Appl. 30.6.63		Farbenfabriken Bayer	Poly(butadiene)	Mixture of styrene and acrylonitrile	25–85% styrene and 10–47% acrylonitrile is graft copolymerised onto 5–50% poly(butadiene). Polymerization is started in not more than 30% of total emulsion of polybutadienes and graft, the remaining 70% being added continuously at a rate controlled by the polymerization rate		846
Neth. Appln	64,07752	Germ. Appl. 11.7.63	12.1.65	Farbenfabriken Bayer	Polymeric conjugated alkadienes	Mixture of styrene and acrylonitrile	Claims thermoplastic copolymer mixtures with good antistatic as well as physical properties prepared from 5–60% of a graft copolymer consisting of 10–80% of a mixture of 50–90% styrene are 50–10% acrylonitrile and 90–20% polymeric conjugated alkadiene	*CA*, 63, 1945	847
Brit.	1,014,019	Germ. Appl. 30.7.63	22.12.65	Farbenfabriken Bayer	Poly(butadiene) latex	Mixture of styrene and acrylonitrile	Claims a process for preparing thermoplastic-elastic moulding compositions by emulsion graft polymerising styrene and acrylonitrile on a butadiene polymer latex		848

Neth. Appln	64,08739	Germ. Appl. 30.7.63	1.2.65	Farbenfabriken Bayer	Equivalent to Brit. 1,014,019		See above	*CA*, 63, 7173	849
Belg.	652,069	U.S. Appl. 20.8.63		Monsanto Chemicals	Polyolefin especially poly(ethylene)	Vinyl halide, e.g., vinyl chloride	Claims polyolefin-vinyl halide graft copolymers prepared by adding to a vinyl halide a finely divided polymerised olefin and polymerizing the vinyl halide by usual methods. The process is especially suitable for the production of poly(ethylene)/vinyl chloride graft copolymers		850
Belg.	652,191	Germ. Appl. 23.8.63		Farbenfabriken Bayer	Copolymer containing ethylene and 20-80% of a vinyl ester of a Cl–8 monocarboxylic acid, preferably 30–70% of vinyl acetate	Vinylidene chloride or a mixture of vinyl chloride and vinylidene chloride preferably containing 20–95% of vinylidene chloride	Graft copolymers with film-forming properties are prepared by mixing said monomer mixture with a preformed ethylene-vinyl acetate copolymer in the presence of a free radical catalyst. The quantities of monomers used are such that the graft copolymer contains 10–95% of the monomers. Polymerization is preferably carried out in aqueous suspension at 10–100°C		851
Belg.	652,120 (addn to Belg. 636,977)	Germ. Appl. 23.8.63		Farbenfabriken Bayer	Copolymer of ethylene and 20–80% of a vinyl ester of a C1–8 monocarboxylic acid, preferably 30–70% vinyl acetate	Monomer mixture comprising vinyl chloride and other comonomers chosen from esters formed by monoolefinic carboxylic acids containing 3 or 4 C atoms with unsaturated C1–18 monoalcohols	Claims graft copolymers formed by subjecting to free radical polymerisation, a preformed copolymer of ethylene and a vinyl ester of a C_{1-8} monocarboxylic acid, and a monomer mixture comprising vinyl chloride and other comonomers		852

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Fr.	1,405,656	Germ. Appl. 23.8.63		Farbenfabriken Bayer	Equivalent to Belg. 652,120		See above		853
Belg.	652,054	Germ. Appl. 27.8.63		Farbenfabriken Bayer	Partially hydrolyzed copolymer of ethylene and a vinyl ester of a carboxylic acid	Vinyl chloride	Claims a hard, shock-resistant graft copolymer prepared by grafting vinyl chloride onto a partly hydrolyzed copolymer of ethylene and a vinyl ester of a carboxylic acid. The graft copolymer contains 5–70% of the partially saponified copolymer, and the latter contains 30–70% vinyl ester, 10–80% of the ester group being transformed into hydroxyl groups		854
USSR	165,537	23.9.63	12.10.64		Poly(methacrylic acid)	ε-caprolactam	Poly(methacrylic acid) and ε-caprolactam are graft copolymerized at 80° to give copolymers with a closed caprolactam ring	*CA*, 62, 5359	855
Fr.	1,415,030	U. S. Appl. 17.10.63		Monsanto Chemicals	Copolymer of a conjugated diene and an unsaturated ethylenic monomer	A mixture of an ethylene nitrile and an unsaturated copolymerizable ethylenic monomer	Claims a graft copolymer comprising 100 parts of a diene rubber polymer base per 15–200 parts of a hydroxylated polymer forming the "top layer"		856
Neth. Appln	299,793	25.10.63	25.8.65	Koninklijke Industrieele Maatschappij	Copolymers containing 0.05–20 parts of an α-β unsaturated peroxy ester	Styrene, vinyl esters, acrylic or methacrylic derivatives, or acrylonitrile	Graft copolymers of good mechanical properties are prepared from monomers such as styrene and copolymers made from 100 parts of a monomer and 0.50–20 parts of an α-β unsaturated preoxy ester	*CA*, 64, 836	857
Neth. Appln	64,11609	Germ. Appl.	27.4.65	Nitrochemie	Cellulose	Anhydride of a $C4^+$ polybasic	Cellulose or its derivatives are treated with the anhydride of a	*CA*, 63, 15095	858

		26.10.63				acid	$C4^+$ polybasic acid in the presence of an organic base. The preferred ratio of base to anhydride is 1:1; application of 0.3–50% of this mixture determines the degree of hardness of the end product		
Neth. Appln	64,12812	U. S. Appl. 4.11.63 27.1.64	6.5.65	Esso Research and Engineering	Terpolymer containing at least 20% ethylene, at least 15% C3–10 aliphatic α-olefin, and 0.01g-mol. per 100 gm. of terpolymer, but not more than 20%, of a non-conjugated C6–15 diolefin	Ethylenically unsaturated compound polymerizable by free radicals	Sulfur-vulcanizable graft copolymers are prepared by polymerising an ethylenically unsaturated monomer in the presence of said terpolymer mixture	*CA*, 63, 13542	859
Brit.	1,015,236	6.11.63	31.12.65	Drayton Research	Chloroprene polymer, a butadiene-styrene copolymer or natural rubber	Mixtures of one or more of styrene, acrylonitrile methyl acrylate or methyl methacrylate	Graft copolymers suitable as insulants are prepared by polymerizing said monomer mixture together with an unsaturated polyester resin and trichloroethylene upon a polymeric component comprising a chloroprene polymer, a butadiene-styrene copolymer or natural rubber		860
USSR	166,443	20.11.63	19.11.64		Cellulose	Methacrylic acid ester, e.g., heptamethyl-trisiloxanyl methyl methacrylate	Fibres with water-repelling properties are produced by grafting a methacrylic acid ester onto cellulose		861
Fr.	1,414,477	Ger. Appl. 27.11.63		Chemische Werke Hüls	Poly(butadiene)	Styrene	Claims shock-resistant styrene graft copolymers containing more than 80% of the butadiene in the 1,4-*cis* form		862

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Fr.	1,385,548	3.12.63	15.1.65	Produits Chimiques Pechiney-Saint-Gobain	Chlorinated butyl rubber	Vinyl chloride	Graft copolymers of good impact strength are prepared by bulk polymerization of vinyl chloride in the presence of a catalyst and a chlorinated butyl rubber	*CA*, 62, 11935	863
Belg.	657,762	U. S. Appl. 30.12.63		Monsanto Chemicals	Polyolefin	Vinyl halide monomer	Claims graft copolymers prepared by dissolving a polyolefin in a vinyl halide monomer at elevated temperatures and pressures and polymerizing the vinyl halide by conventional methods		864
Neth. Appln	64,15317	U. S. Appl. 3.1.64	5.7.65	California Research Corp.	(Process claim) Isotactic poly(propylene)	4-vinylpyridine	An aqueous dispersion of a polymer containing a surfactant and one or two vinyl monomers is heated in the presence of a free-radical catalyst to give a graft copolymer of improved dyeability without effect on the other characteristics of the polymer	*CA*, 64, 864	865
Neth. Appln	65,00146	Ital. Appl. 9.1.64 14.12.64	12.7.65	Montecatini	Saturated ethylene-α-olefin copolymers or a lower unsaturated olefin terpolymer, e.g., ethylene-propylene-1,5-cyclooctadiene terpolymer	Water soluble acid vinyl or vinylidene monomer, e.g., acrylic or methacrylic acid	Aqueous latexes of a saturated ethylene-α-olefin copolymer or a lower unsaturated olefin terpolymer containing anionic surfactants are grafted with a water soluble acid vinyl or vinylidene monomer in the presence of a radical initiator. The resulting latexes are very stable	*CA*, 64, 5229	866
Belg.	659,430	Germ. Appl. 8.2.64		Farbwerke Hoechst	Polymers or copolymers of halogenated com-	Vinyl monomers, e.g., vinyl chloride, styrene,	Graft copolymers are prepared by polymerising said monomer in aqueous emulsion to a conversion		867

					pounds. The halogen atoms are preferably activated by one or more electronegative groups	alkyl (meth)-acrylate having C1–8 alkyl group, and/or acrylonitrile	of 60%, then introducing the backbone polymer containing active halogen and polymerizing the mixture under the action of UV light and high energy particles until at least 90% conversion has occurred		
Pol.	49,401	10.2.64	15.5.65	Instytut Badan Jadrowych, Poleskiej Akademi Nauk	Terephthalic acid polyesters	Vinylpyridine	The dyeing of terephthalic acid polyester fibers is improved by grafting with vinyl pyridine initiated by ionising or UV radiation	*CA*, 64, 5247	868
Fr.	1,394,915	25.2.64		Produits Chimiques, Pechiney. Saint-Gobain	Chlorinated butyl	Vinyl chloride	Claims a polymer blend based on PVC and PVC-chlorinated butyl rubber graft copolymer		869
Neth. Appln	65,02357	Fr. Appl. 25.2.64		Produits Chimiques Pechiney. Saint Gobain	Equivalent to Fr. 1,394,915		See above		870
Belg.	660,860	Brit. Appl. 13.3.64	9.9.65	Imperial Chemical Industries	Poly(methylmethacrylate)	Lauryl methacrylate	Graft copolymers, which are prepared by dispersion polymerization in a low boiling solvent (which dissolves the monomer but does not dissolve the polymer), are treated with a high boiling solvent (b. 100°) (in which the polymer is soluble) and the low boiling solvent is distilled off to give solutions which can be used as coating compositions	*CA*, 63, 18478	871

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
Fr.	1,411,704	29.4.64		Kleber Colombes	Polyolefins	Ethylenic monomer	Claims cross-linked cellular polyolefins containing 1–100 parts of a polymerizable compound having at least one ethylenic or cycloalkenic double bond grafted onto 100 parts of the polyolefin	872
Belg.	663,290	U. S. Appl. 1.5.64		Allied Chemical Corp.	Chlorinated-poly(ethylene)	Vinyl monomer	Claims graft copolymers prepared by heating a chlorinated ethylene polymer, which has activated sites for free-radical polymerization, with at least 5% by wt of a vinyl monomer	873
Belg.	663,786	U. S. Appl. 12.5.64		General Aniline and Film Corp.	*N*-vinyl-lactam polymer	Vinyl monomer chosen from vinyl or isopropyl acetate; vinyl laurate, stearate, oleate, benzoate or chloride; 2-chloroprene; methyl, ethyl or isopropyl vinyl ethers; methyl or ethyl acrylate; methyl methacrylate 2-ethylhexyl or hexyl acrylate; styrene and methoxymethyl—or chloro-styrene	Claims graft copolymer prepared by reacting 5–60 parts *N*-vinyl-lactam polymer with 95–40 parts of a nonaqueous vinyl monomer in the presence of a free radical catalyst and an aerosol propellent. Some of the products are suitable for hair sprays	874
Belg.	663,603	Germ. Appl.		Farbenfabriken	Ethylene-vinyl ester copolymer	Monomer mixture comprising 60–	Claims graft copolymers prepared by grafting upon an ethylene-vinyl	875

		14.5.64	Bayer	(preferably acetate)	95% vinyl chloride, 0–40% α-β-unsaturated mono- or dicarboxylic acids or derivatives thereof, and/or 0–40% vinyl ester	acetate copolymer (containing 40–75% vinyl acetate) and in which 10–60% of the acetyl groups are hydrolysed, said monomer mixture with the aid of usual polymerisation inducers	
Belg.	663,931 (addn to Belg. 636,977)	Ger. Appl. 15.5.64	Farbenfabriken Bayer	Copolymer of ethylene and vinyl acetate	Vinyl chloride	Claims the free-radical polymerisation of vinyl chloride in the presence of a copolymer of ethylene and a vinyl ester (which contains lower alkyl or aryl groups) the ratio of aqueous phase to the sum of the grafting substrate and the grafting monomer being maintained between 1.5:1 and 0.5:1. 0.01 to 1% activator is necessary	876
Irish Appln	680/64	Brit. Appl. 5.6.64 6.8.64	Imperial Chemical Industries	Polymer containing a terminal functional group, e.g., carboxyl, hydroxyl, amine or substituted amine	Ethylenically unsaturated monomer	A process of making addition polymers containing a terminal functional group reactible in a condensation reaction is claimed by polymerising an ethylenically unsaturated monomer in the presence of an initiator and a chain transfer agent, each of which contains said functional groups. A process of making a block or graft copolymer by reacting in a condensation reaction a terminal functional group contained in a polymer made by the above process with a complementary functional group contained in another polymer is also claimed	877

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference
Neth. Appln	65,07279	U. S. Appl. 8.6.64		General Aniline and Film Corp.	*N*-vinyl-lactam polymer, e.g., poly(*N*-vinylpyrrolidone)	Acrylic ester, e.g., methyl methacrylate	Claims a diazo material comprising a base coated with an aqueous dispersion of a graft copolymer of a *N*-vinyl lactam and an acrylic ester containing a light sensitive diazonium compound	878
Belg.	665,220	Germ. Appl. 10.6.64		Chemische Werke Hüls	Rubbery co- or terpolymers of monoolefine, e.g., ethylene-propylene-biscyclopentadiene polymer (50:45:5)	Styrene or styrene in admixture with other copolymerisable monomers, e.g., styrene-ethyl acrylate	Claims impact-resistant styrene graft copolymers prepared by polymerizing styrene alone or with other copolymerizing monomers, on a rubbery copolymer of monoolefins in aqueous suspension in the presence of stabilising agents and catalyses soluble in the monomers	879
Belg.	664,090	Germ. 11.6.64		Farbenfabriken Bayer	Ethylene-vinyl-acetate copolymers	Vinyl and/or vinylidene chloride	Graft copolymers of unsaturated compounds, e.g., ethylene-vinyl acetate copolymers are prepared by first swelling the copolymer in an unsaturated liquid as an aqueous dispersion. The gels thus obtained are polymerized with free-radical catalyses at 5–60°C or preferably 15–50°C. Homogeneous grafts are obtained and the products can be separated from the aqueous phase and dried	880
Belg.	665,479	U. S. Appl. 17.6.64		Union Carbide Corp.	Poly(acrylonitrile), PVC, poly(styrene), poly(propylene), natural rubber and	Gum-arabic, hydroxyethycellulose, polycarbonate resins of	Claims polymeric polyols containing Zerewitinoff active hydrogen, containing 0.5–50% prepolymer, preferable 0.5–30% poly(urethane), of	881

					copolymers of vinyl chloride and vinyl acetate	2,2-bis(hydroxyphenyl)propane, polychloroethers, phenol-formaldehyde resins or polyhydroxy ether resins	which a small amount is grafted onto the polyol		
Belg.	649,464	U. S. Appl. 18.6.64		Union Carbide Corp.	Poly(alkyl acrylate)	Butadiene	Claims polymer blends of poly(vinyl chloride) and 0.5–50% graft copolymer of butadiene-alkyl acrylate. 10–185% methyl methylate can be further grafted onto the copolymer		882
Fr.	1,399,201	U. S. Appl. 19.6.64		Union Carbide Corp.	Copolymer of butadiene and alkyl acrylate	Methyl methacrylate	Claims polymer blends of poly(vinyl chloride) and a graft of methyl methacrylate on a butadiene-alkyl acrylate copolymer. Numerous variants of the above type of blend are also claimed		883
Fr.	1,399,515	26.6.64	14.5.65	Scientific Research Institute of Synthetic Resins	Cellulose or its derivatives	Unsaturated monomer	Cellulose or its derivatives are activated at 40–140° for 5–40 min by treatment with a substance capable of introducing free-radicals therein, and treated with 50–300% (by wt. of cellulose) of an unsaturated monomer, precipitated with water to form a two-phase polymerisation system and mixed for 1–8 hr at 50–60°C	*CA*, 64, 3833	884

APPENDIX III

Appendix III includes some of the early foreign patents for which the application date is not readily available. These patents are grouped in order of the publication date. The codings and abbreviations are as for Appendix II.

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Brit.	507,323			Standard Telephones and Cables	Poly(isobutenes)	Styrene, divinyl benzene	Poly(isobutenes) with molecular weights from 100,000–200,000 are dissolved in monomers by heating and then heated at 120°C for 2 days to graft copolymerize. Light milling is used to homogenize the products	Ceresa, p. 112	885
Dutch	65,127		15.2.50	Indonesisch Instituut Voor Rubber onderzoek	Natural rubber	Vinyl compounds composed of unsaturated aliphatic hydrocarbons with at most 6 carbon atoms in the unsaturated chain or their substitutes having 1 or more electronegative or aromatic substituents attached to the unsaturated chain	Oil-resistant derivatives of natural rubber are prepared by reacting the rubber with vinyl compounds in the presence of a catalyst at a temperature below 70° preferably between 30° and 40°	*CA*, 44, 4279	886

Fr.	972,455	30.1.51	Societe Auxiliare de L'Institut Francais du Caoutchouc	Natural rubber	Vinyl monomer, e.g., acrylonitrile styrene or butyl methacrylate	Rubber is reacted with a vinyl monomer in an aqueous emulsion in the presence of an emulsifier, a protective colloid, and a polymerization catalyst. The graft copolymer so formed may be vulcanized	*CA*, 46, 8889	887
Fr.	972,456	30.1.51		Natural rubber	Ethylenic compounds, e.g., acrylic acid, acrylonitrile, maleic andydride, and styrene in amounts from 1–15% of the rubber	Ethylenic compounds are masticated, on hot or cold rollers, with natural rubber to give a more insoluble rubber. A peroxy catalyst may be added, as may inhibitors		888
Dutch	75,532	16.8.54	N.V. De Bataafsche Petroleum Maatschappij	Vinyl-type polymers, e.g., poly (methyl methacrylate)	Vinyl chloride or other vinyl monomers	Vinyl-type monomers are polymerized under such conditions that polymer nuclei are formed, which continue to exist as long-lived free radicals, and after approx. completion of this initial polymerization a second monomer is introduced while polymerization is continued but now under such conditions as to form no other active polymer nuclei	*CA*, 49, 5884	889
Fr.	1,101,682	10.9.55	Polyplastic	Natural rubber	Acrylic acid, acrylonitrile or styrene	A solution or emulsion of one or more polymers containing double links is peroxidized or ozonized, and the decomposition of the product obtained indicates the polymerization of one or more monomers to form a graft copolymer with improved properties	*CA*, 53, 14569	890

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
Ital.	564,711		27.6.57	Montecatini	Poly(propylene) or its copolymers	Vinyl or vinylidene compounds e.g., methyl methacrylate or acrylate	Films or yarns of poly(propylene) or its copolymer are subjected to an almost superficial or deeper peroxidation at 60–120° by O or O-contg. gas mixtures at 1–10 atm. The products are subjected to further reaction and polymerization of the peroxidized surface at 50–80° with gaseous liquid, or dissolved monomers which are grafted on the linear polymer chains	*CA*, 53, 15646	891
Ital.	565,618		27.7.57	Montecatini	The process described in Ital. 564,711 (see above) is modified by using a monomer mixture containing vinyl and (or) methallyl esters of carboxylic acids RCOOH (R is alkyl with 1–2 carbon atoms and is chlorosubstituted) and alkyl methacrylate, acrylonitrile and (or) styrene or a mixture containing vinyl acetate or chloroacetate and methyl methacrylate or acrylonitrile			*CA*, 53, 22981	892
Can.	549,110		19.11.57	Polymer Corp.	Naturally occuring polymers or their derivatives	Butadiene mixed with acrylonitrile or styrene	Graft copolymers of naturally occurring polymers are prepared by oxidising them in aqueous solution or suspension with at least 1 part per 100 polymer of an O_2 containing gas. Any excess oxidant is flushed out with an inert gas, and the monomer is added, usually with a mercaptan modifer, an emulsifier, and an activator	*CA*, 52, 7768	893
Ger.	1,015,226			Hercules Powder	Olefin polymers	Olefin monomers	Claims the production of graft copolymers from an olefin polymer containing a hydroperoxide which produces free radicals, and an olefin monomer		894
Ger.	1,024,240		13.2.58	Rohm and Haas	Poly(alkyl acrylates) containing an	Monomer capable of dissolving or	Graft copolymers are formed by swelling a poly(alkyl acrylate) in	*CA*, 54, 13745	895

				alkyl with preferably 8–≤18 carbon atoms, in which a teritiary carbon atom should not be bound to the carboxylic group	swelling the polymer, e.g., methyl methacrylate	an appropriate monomer and irradiating the mixture to between 500,000–1,000,000 rep. The temperature is limited by the lowest 2nd order transition temperature of the components and favorably higher than the highest of the graft polymers. The upper limit is the temperature where homopolymerization of the monomer sets in		
USSR	111,857	25.6.58	A. A. Berlin, L. V. Stupen, B. J. Fedoseeva, D. M. Yanovskii	Copolymers of the methacrylate series	Vinyl chloride	Graft copolymers are obtained by causing copolymers of the methaacrylate series to react with vinyl chloride. The resulting products have a low inflammability and and improved adhesive properties	*CA*, 53, 772	896
Ital.	580,203	30.7.58	Montecatini	Poly(propylene)	Styrene or 2-methyl-5-vinylpyridine	The poly(propylene) surface is not peroxidized as in Ital. 565,618 (ref. 892) but is coated with a thick layer of a polymerization initiator, such as an aromatic hydroperoxide or an azo compound. The coated polymer is then heated in the absence of air with the said monomer	*CA*, 53, 23096	897
Ger.	1,040,249	2.10.58	Union Carbide	Poly(1,3-butadiene)	Styrene and acrylonitrile	Claims polymers from 1,3-butadiene (I), styrene (II), and acrylonitrile (III), with very low brittle points and a good stiffness at 30° as well as at subzero temperatures obtained by grafting dispersions of poly I with II and III	*CA*, 54, 26019	898

(continued)

Country	Number	Application date	Published date	Patentee	Backbone polymer	Grafted monomer	Claim	Reference	
USSR	116,268		19.1.59	V. V. Korshak K. K. Mozgova	Polyamides	Vinyl monomers	Polyamides are treated first with oxygen containing 5% ozone and then with a vinyl monomer. Polyamides thus treated became more adhesive and their mechanical strength increases	*CA*, 53, 19460	899
USSR	118,976		25.3.59	G. L. Yukhnovskii, A. V. Chernobai	Poly chloropentadiene	Monomeric esters of acrylic and methacrylic acids	Claims film-forming resins obtained by polymerizing monomeric esters of acrylic and methacrylic acids in the presence of polychloropentadiene	*CA*, 53, 23106	900
Brit.	834,557		11.5.60	Du Pont	Synthetic or natural fiber textiles	Specific monomers, e.g., methoxy-nonaethyleneoxyethyl methacrylate	X-ray doses are given to synthetic or natural fiber textiles in the presence of Al-foil wrappers and impregnated protective materials, such as poly(ethylene glycol), or organic modifiers which can react with the textile material to give a modification of properties	*CA*, 54, 25870	901
USSR	131,084		20.8.60	K. K. Mozgova, V. V. Korshak, M. A. Shkolina	Polyamides or polyesters	Vinyl monomers	Polyamides or polyesters preheated to 80–90° are treated with vinyl monomer at 65–80° to form graft copolymers with improved properties	*CA*, 55, 6048	902

APPENDIX IV

Appendix IV lists in alphabetical order the patentees of graft copolymers together with the number of main and equivalent patents held by each.

Patentee	Main	Equivalent
L. Adany	1	
Adhesive Tapes	2	
Advance Solvents	1	
Agency of Industrial Science and Technology	1	
Allied Chemical Corporation	1	
American Cyanamid	12	(6)
American Machine and Foundry	3	
American Viscose Corporation	1	
R. Aries	1	
Ashi Chemical Industries	3	
Atlas Chemical Industries	1	(2)
Badische Anilin und Soda Fabrik (B.A.S.F.)	18	(4)
Basdekis, C. H., Prill, E. J., and Walker, G. E.	1	
Beck	1	
Borg-Wagner	11	(5)
British Rubber Producers Research Association	4	
O. W. Burke, Jr.	5	(1)
B. X. Plastics	22	(4)
California Research Corporation	1	
Canadian Industries Ltd. (C.I.L.)	1	
Catalin Corporation	1	
Centre National de la Recherche Scientifique (C.N.R.S.)	12	(12)
C.N.R.S. and Dow Chemical	1	
Chemische Werke Hüls	7	(3)
R. H. Cole	1	
Chemstrand Corporation	3	
Colgate-Palmolive	1	
Compounds Research Association	1	
Continental Can	1	
Cosden Petroleum Corporation	3	
Courtaulds	1	
Czech Patents	4	
Dainippon Spinning	2	
De Bell and Richardson	1	

(continued)

Patentee	Main	Equivalent
Deutsche Gold and Silber Scheideanstalt	2	
Drayton Research	1	
Distillers	8	(5)
Dow Corning—Midland Silicones	3	(3)
Dow Chemicals	70	(2)
Dunlop Rubber	5	
Du Pont	43	(20)
Dynamite-Nobel	1	
Eastman Kodak	29	(2)
Esso Research and Engineering	10	(5)
Ethylene-Plastique	5	(2)
Farben-Fabriken Bayer	22	(5)
Farbwerke Hoechst	21	(2)
Firestone Tyre and Rubber	9	
FMC Corporation		(1)
Foster-Grant	1	
Furukawa Electric	1	
General Aniline and Film Corporation	4	(1)
General Electric	1	(2)
General Tyre and Rubber	4	(3)
B. F. Goodrich	2	(2)
Goodyear Tyre and Rubber	1	(2)
W. R. Grace	10	(1)
Haris Kabushiki Kaisha	2	(2)
Heberlein	3	(1)
Hercules Powder	2	
A. Hemeryck	1	
Houilleres	5	(4)
Imperial Chemical Industries (ICI)	15	(1)
Indonesisch Instituut Voor Rubberonderzoek	1	
Industrial Research Institute, University of Chattanooga	1	
Instytut Baden Jadrowych, Poleskiej Akademi Nauk	1	
Interchemical Corporation	3	
International Synthetic Rubber	3	(2)
Israeli Patents	1	
Japan Carbide Industries	1	
Japanese High Polymer Radiation Research Association	10	
Japan Rayon	2	
Japan Telegram and Telephone Corporation	1	
Kabushiki Kaisha Hitachi Seisakusho (Japan)	1	
Kanegafuchi Spinning	1	
Kani Chemical Industry	1	
Kibernia Chemie	1	

(continued)

Patentee	Main	Equivalent
Kleber-Colombes	9	
Koninklijke Industriele Maatschappij	1	
Koppers	4	
Kulzer & Co.	1	
Kurashiki Rayon	1	
Kureha Chemical Industry	1	
Kureha Spinning	1	
W. H. Kreidl	1	
Licenta Patent-Verwaltung	1	
A. D. Little Inc.	1	
Mauanyagipari Kutato Instezet (Hungary)	1	
Mazzucchelli Celluloide	1	
Metallgesellschaft	2	
Midland Silicones	2	
Minnesota Mining and Manufacturing	2	(1)
Monsanto	28	(7)
Montecatini	22	(8)
National Research and Development Corporation	1	
National Rubber Producers Research Association	2	
National Starch and Chemical Corporation	2	
Nehemia Salomon (Israel)	1	
Nihon Hoshasen Kobunshi Kenkyn Kyokai (Japan)	1	
Nisslin Cotton Spinning	1	
Nitro Chemie	1	
Nitto Chemical Industries	2	
Nobel-Bozel	6	(5)
N. V. de Bataafsche Petroleum Maatschappij	1	
G. Oster	1	(2)
Owens-Illinois Glass	1	
Pechiney Compagnie de Produits Chimiques et Electrometalluriques-Saint Gobain	11	(5)
Petrolite	1	
Phillips Petroleum	4	
Polaroid Corporation	1	
Polymer Corporation	6	(3)
Polyplastic	12	(4)
Polyplastic—Kleber Colombes	1	
Progil S.A.	1	
Rayonier Inc.	2	
Regie Nationale des Usines Renault	1	(1)
Research Institute for Production Development	1	(1)
Rhone-Poulenc	8	(9)
Rubber and Plastics Research Association of Great Britain	1	

(continued)

Patentee	Main	Equivalent
Rohm and Haas	15	(8)
Scientific Research Institute of Synthetic Resins	1	
Scott Paper	2	
Shawinigan Chemicals	6	
Shell Internationale Research Maatschappij	6	(2)
Shin Nippon Chisso Kiryo	2	
Showa Electronic Industry	3	
Sicedison	1	
Smith and Nephew	1	
W. H. Smyers and D. W. Young	1	
Société Auxiliare de L'Institut Français du Caoutchouc	2	
Société D'Electrochimie D'Electrometallurgie et des Acieries Electriques d'ugine	2	(1)
Société Nationale des Petroles D'Aquitaine	1	
Solvic-Cie	3	(3)
A. E. Staley	1	
Standard Oil Development	6	
Standard Telephone and Cables	1	
Styrene Products	2	
Theodore Alcott Tegrotenhuis	1	
Toyo Kagaku	2	
Toyo Rayon	5	
Toyo Spinning	13	(1)
Tube Investments	2	
Union Carbide	19	(3)
United States Rubber	15	(5)
Universal Oil Products	1	
United States Atomic Energy Commission	1	
United States Department of Agriculture	1	
USSR Patents	18	
Van Kohorn Constructora	1	
V. E. B. Chemische Werke Buna	1	
Wingfoot	1	
Yardney International Corporation	3	
Total	728	174

APPENDIX V

Appendix V lists the patent application statistics for Companies holding ten or more patents. The number of main patents applied for by each Company per year is indicated.

Companies holding ten or more graft copolymer patents	Total	<1952	1952	1953	1954	1955	1956	1957	1958	1959	1960	1961	1962	1963	1964
American Cyanamid	12						2	1	3	1	1	2	2		
B. A. S. F.	18								2	3	8	3	2		
Borg-Warner	11				1		1	1	2	1		5			
B. X. Plastics	22							6	3	6	2	5	1		
C. N. R.S.	12					2	3	2	3				1	1	
Dow	70	3				1	6	9	19	17	7	3	4	1	
Du Pont	43	4	1		1	5	9	5	11	2	2	1	1	1	
Eastman Kodak	29	6	5	1	8	3	1		2	3					
Esso	10				1	1	1	1		1	1	3		1	
Farben-Fabriken Bayer	22									1		1	10	7	3
Farbwerke-Hoechst	21								4	2	5	3	5	1	1
W. R. Grace	10									1	5	4			
ICI	15	1	2	1	1	1			1	1	1	1	1	2	2
Japanese High Polymer Research Association	10									2	2	3	3		
Monsanto	28				3		1	5	4	7	2	2		4	
Montecatini	22	2			2		4	5	4	1	2			1	1
Pechiney-Saint Gobain	11						3			2	1	1	2	1	1
Polyplastic	12	1			1		3	3			4				
Rohm & Haas	15	1				1	2		5	2	2	1	1		
Toyo Spinning	13										7	4	2		
Union Carbide	19	2		2	4		4	1	1					2	3
United States Rubber	15			1	1	1		2	2		1	1	6		
USSR	18							1	1	3		4	3	6	

APPENDIX VI

Appendix VI lists the methods utilizing ionizing radiation for the synthesis of graft copolymers. The principle of the method is described together with the various refinements that have been patented or published in the general literature. If available, a reference has been given to the first publication of the refinement. Note that the date given with the patent number refers to the publication date.

A list of references is also given to the patent abstracts of Appendixes II and III which deal with the methods cited.

Principle of method	Refinements	First published in lit.	First patent publication	Reference
		Direct Method		
Grafting is effected by irradiating a preformed macromolecule to form an active site, in the presence of a polymerisable monomer $\begin{array}{l}A{\sim}A\\ \downarrow\gamma\end{array}$	(*a*) The polymer is immersed in an excess of monomer and irradiated in the absence of oxygen	M. Magat, *J. Chim. Phys.*, 52, 709 (1955); L. Bouby, A. Chapiro, M. Magat, E. Migirdicyan, A. Prevot-Bernas, L. Reinisch, and J. Sebban *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva*, 1955. United Nations, 1956, Vol. VII p. 526	Centre National de la Recherche Scientifique. Brit. 801,528, (Sept. 17, 1958)	102, (103), (104), (105), 122, 124, (125), (126), 128, 135, 156, 159, (160), 182 183, 187, (188) (189), (190), 200, (201), (202), (203), (204), 225, 229, 230, 247, 250, 253, 266, (267), (268), (269), 302, (303), 360, 370, 373, (374), (375), 398, 500, 521, 522, 557, 558, 581, 598, 621, 634, 649, 654, 696, 725, 734, 766, 820, 844, (845), 868
$\begin{array}{l}A{\sim}A\\ \;\dot{}\\ \downarrow + nB\end{array}$	(*b*) Homopolymer formation is reduced by irradiating the polymer with sufficient monomer to only just swell it		A. Chapiro, M. Magat, and J. Sebban Fr. 1,130,099 (1956) Centre National de la Recherche Scientifique	262,288, 289, (290), (291), 310, (311), (312), 337, 338, 340, 341, 345, 359, 381, 385, 388, 435, 437, 645, 895
$\begin{array}{l}A{\sim}A\\ \wr + B_q\\ B\end{array}$	(*c*) The polymer is irradiated in a monomer solution, the solvent of which may swell the polymer		Du Pont, Brit. 820,120, (Sept. 16, 1959)	89, 93, 94, 276, 348, 378, 417, 427, 520, 526, 556, 623, 624, 639, 671

also $B \xrightarrow{\gamma} R \xrightarrow{+nB} B_q$ (homopolymer)	(*d*) Selective inhibitors are added which reduce homopolymerisation without affecting the grafting process too much		J. Danon, A. Chapiro, and M. Magat Fr. 1,157,006 (May 23, 1958) to Centre National de la Recherche Scientifique	172, (173), (174), (175)
	(*e*) Small amounts of activating agents are added, e.g., hexahydro-1,3,5-triacryloyl-*s*-triazine which make it possible to decrease the amount of irradiation normally necessary for grafting to occur		Societe Nobel Franciaise Fr. 1,171,806 (Jan. 30; 1959)	254, (255), (256), 364
	(*f*) A finely divided inorganic solid is homogeneously dispersed and suspended throughout a mixture of polymer and monomer and the dispersion exposed to the action of ionising radiation		Dow-Corning U. S. 2,959,569 (1960)	168, (169)
	(*g*) The monomer is first polymerised to about 84% conversion with a chemical free radical initiation and then added to the polymer and irradiated *in vacuo*		Minnesota Mining and Manufacturing U. S. 3,068,187 (Dec. 11, 1962)	497, (498)
	(*h*) Addition of a nonsolvent for the polymer chains being formed can increase considerably the rate of grafting	G. G. Odian, A. Rossi, and H. Trachtenberg, *J. Polymer Sci.*, 42, 575 (1960); G. G. Odian, A. Rossi and K. Klein, 138th Meeting American Chemical Society, New York, 1960	United States Rubber Austal. Appln. 2,071/61	567, 707, 722

(continued)

Principle of method	Refinements	First published in lit.	First patent publication	Reference
	(*i*) The polymer is first swollen in a monomer capable of graft copolymerizing therewith and then immersed in a second liquid which is a solvent for neither the polymer nor the monomer. The mixture is then subjected to the action of ionizing radiation		Nobel-Bozel Fr. 1,210, 101	400, (401), (402)
	(*j*) For diffusion controlled reactions, grafting may be enhanced by allowing the monomer to diffuse into the polymer between bursts of irradiation	A. Charlesby, and S. H. Pinner, *Ind. plastiques Mod. (Paris)*, 9, No. 10, 43 (1957)	Saint-Gobain Fr. 1,147,722 (Nov. 28, 1957)	143, (144), (145), 350
	(*k*) Surface grafts are obtained when a polymer in contact with a polymerizable monomer is irradiated under conditions in which swelling is substantially absent	J. Behr, R. B. Mesrobian A. J. Restaino, D. S. Ballantine, A. Glines, and D. J. Metz, *J. Polymer Sci.*, 21, 219 (1956)	Heberlein Austrln. Appln. 59,118/60 (April 11, 1963)	487
	(*l*) An embedded graft is obtained by allowing the monomer to swell the polymer to the desired depth followed by irradiation in the presence of an inhibitor; e.g., O_2. The graft is thus inhibited on the surface zone, the thickness of which is determined by the time allowed for the diffusion of the inhibitor, while the inner part is grafted	A. Henglein and W. Schnabel, *Makromol. Chem.*, 25, 119 (1957); A. Henglein, W. Schnabel, and K. Heine, *Angew, Chem.*, 70, 461 (1958).		
	(*m*) The polymer is subjected to ionizing radiation in the presence of a grafting monomer, the		Centre National de la Recherche Scientifique Belg. 572,100 (1959)	298, (299), (300)

polymer being such that it is not easily penetrated by the monomer, and operating conditions being arranged so that the rate of polymerization of the monomer is lower than the rate of penetration of the monomer in the course of grafting			
(*n*) Monomers are grafted into solid polymers by irradiating the polymers in contact with the monomer vapor		Societe des usines chimiques Rhone-Poulenc Fr. 1,181,893 (1959)	232, 283, (284), (285), (286), 356, 755, 771
(*o*) The grafting process is controlled by mixing the monomer vapor with one or more vaporized substances which increase or decrease the penetration of the monomer into the solid polymer, e.g., water vapor		Societe des usines chimiques Rhone-Poulenc Fr. addn. 73,034 (Sept. 22, 1960)	313, 660
(*p*) Formation of homopolymer may be prevented by maintaining during the irradiation a temperature sufficiently low so that the monomer to be grafted cannot polymerize	J. Zimmerman, *J. Polymer Sci.*, **44**, 107 (1960)	Saint-Gobain Fr. 1,288,829 (March 30, 1962)	646
(*q*) Graft copolymerization of vinyl compounds onto natural or regenerated high polymers can be effectively carried out by irradiating in the presence of a metal cation such as Sn^{2+}, Sn^{4+}, Ti^{3+}, Pb^{2+}, Co^{2+}, Mn^{2+}, and Cr^{2+}		Dainippon Spinning Japan 18,980(64) (Sept. 4, 1964)	712

(*continued*)

Principle of method	Refinements	First published in lit.	First patent publication	Reference
		Preirradiation in Air		
The irradiation of a polymer Ap in the presence of oxygen leads to the formation of a peroxidised polymer ApO_2. The latter can be used in a subsequent reaction for initiating the polymerisation of a monomer and this leads to the formation of a graft copolymer	(*a*) The polymeric peroxides and hydroperoxides that are formed when a polymer is irradiated in air are decomposed thermally at about 60–70° in the presence of monomer	M. Magat, *J. Chim. Phys.*, **52**, 709 (1955); L. Bouby, A. Chapiro, M. Magat, E. Migirdicyan A. Prevot-Bernas, L. Reinisch, and J. Sebban, *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva*, 1955, United Nations, 1956, Vol VII, pp. 526	A. Chapiro, M. Magat, and J. Sebban Fr. 1,125,537; 1,130,100 (1956) to Centre National de la Recherche Scientifique	95, (96), (97), 139, 157, 161, 187, (188), (189), (190), 195, (196), (197), 200, (201), (202), (203), (204), 225, 228, 264, 354, 370, 389, (390), (391), 420, 439, 441, 471, (472), 477, 555, 561, (562), (563), 623, 627, (628), 636, 638, 654, 674, 761, 835
	(*b*) The grafted polymer prepared by the above method is recovered while it still contains active centers and thereafter contacted with another monomer to form further grafted branches,		Centre National de la Recherche Scientifique Brit. 853,970 (addn to Brit. 809,838) (1958)	170, (171), 198
	or The active polymer may be reacted with at least two mutually dissimilar monomers simultaneously		Houilleres, Fr. 1,160,107 (July 8, 1958)	199, 582
	(*c*) The polymer is irradiated as a melt or in solution followed by monomer addition		Ethylene-Plastique Fr. 1,334,305 (Aug. 9, 1963)	301
	(*d*) The polymer is first preirradiated in air with γ-rays from Co^{60}, then dipped in the monomer and further irradiated with UV light at less than 30° C		Showa Electrical Industries Japan 11,437 (62) (Aug. 18, 1962)	565

(*e*) The polymeric substrate is irradiated in air at ≤ 70° and is then contacted with an aqueous dispersion of the monomer. The aqueous phase contains a catalyst, e.g., $Fe^{2+}Ti^{3+}$, or Hg^+, salts, to initiate free radical formation from the peroxides or hydroperoxides.	Atlas Chemical Industries Belg. 629,203 (Feb. 13, 1963)	718, 723, 729, (731)
(*f*) The degradation of the initial polymer is decreased during the irradiation of the reaction mixtures by addition of oxidation preventing agents, such as alcohol, phenol, or amine. A product providing free radicals under the action of the radiation is also added; solvents for the polymer such as CH_3Cl or CCl_4 are preferably used	Du Pont U. S. 2,907,675 (Oct. 6, 1959)	106, 399
(*g*) Homopolymer can arise during the grafting process by the dissociation of low molecular weight peroxides, which may be present in the irradiated polymer. In such an event the extraction of the irradiated polymer by a proper solvent prior to the grafting reaction can prove helpful	R. R. Smith, D. C. McMillanMann and J. F. Salmon Brit. 871,572 (1961); Fr. 1,214,892 (1959) to B. X. Plastics	279, (280), (281)

(continued)

Principle of method	Refinements	First published in lit.	First patent publication	Reference
	(*h*) There is a competition between the rate at which the radicals formed by decomposition of the peroxide react among themselves and the rate at which they react with the monomer. If the temperature at which the peroxidised polymer/monomer mixture is heated is too high, most of the radicals formed by decomposition of the peroxide will recombine before the monomer has time to diffuse through the thin layer of graft copolymer formed on the surface	Shinohara and Tomisha *J. Polymer Sci.*, 44, 195 (1960)		
	Preirradiation in vacuo, Trapped Free Radical Technique			
Irradiation of polymers leads to the formation of radicals. Some of these radicals are trapped in the polymer and can be used to initiate copolymerization	(*a*) The polymer is irradiated *in vacuo* and brought into contact with a liquid monomer which can diffuse into the polymer and thus reach the trapped radical sites	L. A. Wall and D. W. Brown, *J. Res. Natl. Bur. Std.*, 57, 131 (1956) J. C. Bevington and D. E. Eaves, *Nature*, 178, 1112 (1956) A. Chapiro, *J. Chim. Phys.*, 53, 895 (1956); D. S. Ballantine, P. Colombo, A. Glines, B. Manowitz, and D. J. Metz, B. N. L. Report. 414 (T-81) (1956); P. Alexander and A. Charlesby, "Radiobiology Symposium", p. 49, Butterworths, London, 1955	G. Oster Brit. 856,884 (1958); Centre National de la Recherche Scientifique Ger. 1,086,047 (addn. to Ger. 1,070,825)	184, (185), (186), 239, 568, 583, 689

	P. Allen, J. Downer, G. Hastings, H. Melville, P. Molyneux, and J. Urwin, *Nature*, 177, 910 (1956)		
(*b*) This method of grafting depends directly on the efficiency of radical trapping. In general the lifetime of the trapped radicals is much longer at low temperatures; accordingly irradiation at low temperatures increases the grafting yield		Du Pont Ital. 604,774 (1957)	131, 362, (363), 566
(*c*) The irradiated polymer is exposed to monomer vapor rather than liquid	J. Bevington and D. Eaves, *Nature*, 178, 1112 (1956)		
(*d*) If grafting is desired on the surface of a shaped polymer article, the yield of formation of trapped radicals can be increased by irradiating the polymer in the presence of a properly selected fluid in which "active" free radicals are formed under irradiation. These active radicals, e.g., OH, Cl, etc., are then capable of abstracting hydrogens or other atoms from the polymer surface, thus creating polymeric radicals by an indirect effect		H. G. Le Clair, Belg. 549,388; Fr. 1,155,579(1957) Brit. 801, 531(1958) to Du Pont N. G. Gaylor, Belg. 549,387(1957) to Du Pont	107, (108)

(continued)

Principle of method	Refinements	First published in lit.	First patent publication	Reference
	(e) The polymer is first irradiated to a specified dose in the absence of oxygen whereby active centers are formed on the polymer molecule. Within 5 min of irradiation at least a portion of the so formed active centers on the polymer are contacted with oxygen and the oxygenated polymer so formed is then reacted with a monomer capable of being polymerised by free radicals		Centre National de la Recherche Scientifique and Dow Chemicals Brit. 894,753(1961)	454

Interlinking Of Two Different Polymers

Principle of method	Refinements	First published in lit.	First patent publication	Reference
The combination of two polymeric free radicals formed by the irradiation of an intimate mixture of two polymers can lead to graft copolymerisation	(a) To favor the combination of the two polymeric fragments formed during the radiolysis, the polymer modecules must be in very close contact. This may be achieved either by mixing both polymers mechanically at ordinary temperatures or better on hot rollers		A. Charlesby and S. H. Pinner Brit. 805,897 (1958) to T. I. Limited; C. Wippler, Fr. 1,166,793 (1958) to Societe anonyme des Manufactures Des Glaces et Produits Chimiques de Saint-Gobain	
	(b) Or else by evaporating a mixed solution of both polymers in a common solvent	D. Ballantine, P. Colombo, A. Glines, B. Manowitz, and D. Metz, BNL report 414, (T-81) 1956		
	(c) Alternatively the grafting reaction may be carried out in solution	A. Henglein, *Makromol. Chem.*32, 226 (1959)	A. A. Miller, Fr. 1,168,117 (1958) to Compagnie Francaise Thomson-Houston	

Emulsion Techniques

Working in emulsion systems overcomes the difficulty of using heterogeneous systems to prepare graft copolymers. The copolymerization may be initiated by free radical sites formed on the backbone as a result of several reactions, (*a*) direct action of irradiation on the polymer, (*b*) removal of a hydrogen atom from the polymer by the OH radicals produced by the irradiation of the aqueous phase, (*c*) chain transfer, (*d*) formation of buried polymer radicals	(*a*) The monomer is polymerized by an emulsion technique to about 20% conversion, additional monomer is added, and the mixture is further irradiated to initiate copolymerization	K. Shinohara, A. Amemiya, M. Matsumoto, Y. Shinohara, and S. Ohnishi, *Proc. Intern. Conf. Peaceful Uses Atomic Energy Geneva*, 1958.. United Nations, Vol. 29, p. 186	Esso Research and Engineering Brit. 831,833 (1958)	177, 213, (214), 277, (278), 287, 292, 333, 351, 495, 496, 615, 727, 867
	The grafting of methyl methacrylate onto rubber latices was studied by two groups of investigators	W. Cooper, G. Vaughan, S. Miller, and M. Fielden, *J. Polymer Sci.*, 34, 651 (1959); E. G. Cockbain, T. D. Pendle, and D. T. Turner, *Chem. Ind.* (*London*), 759 (1958) D. J. Angier and D. T. Turner, *J. Polymer Sci.*, 28, 265 (1958) *Occlusion method*		
Monomers are incorporated in the polymer latice prior to irradiation	With cellulose for example, vinyl monomers may be induced into the polymer latice by first swelling the cellulose in water and alkali, extracting the water with methanol and benzene and finally replacing the benzene with styrene	R. Huang, B. Immergut, and W. H. Rapson, 138th Meeting American Chemical Society, New York, 1960		

APPENDIX VII

Appendix VII gives a list of references to methods other than radiation for the synthesis of graft copolymers. A brief note on the principle of the method is included together with a reference number to the appropriate abstract in Appendixes II and III.

Method	References
1. Chain transfer reactions	
An active site capable of initiating block and graft copolymerization may be formed on a polymer via a "chain transfer" step in vinyl addition polymerizations.	
(*a*) Transfer to Polymer. If in a system containing polymer P and growing chains of monomer M, chain transfer to P (i.e., abstraction of an atom such as H, or halogen, from P) occurs by the growing chains of M units, polymerization of the monomer can take place at these newly formed reactive sites. The product is a graft copolymer.	3, 6, 7, 15, 17–27, 30–35, 38–43, 45, 54–57, 59, 61, 62, 66–72, 76–84, 86, 92, 98, 109, 118–121, 123, 129, 132, 136–138, 146, 151–153, 162, (163), 191, 192, 209–212, 227, 235, 237, 248, 249, 251, 294, (295), 325, (326), 329, 349, 367, (368), 371, 376, 380, 382, 392, 395, 403, (404), 414, 423, 426, 429, 431, 433, 438, 440, 443–450, 455–457, 460–462, 465, 466, 469, (470), 474–476, 478–481, 483, 485, 486, 488, 490, 491, 494, 501, 506, 508, 513, 523–525, 541–543, 545–548, 550, 553, (554) 559, 569, 570, 572, 576–578, 585, 594, (595), (596), 597, 599, 602, 605, 606, 608, 609, 612, 614, 616, 631, 632, 637, 640–643, 647, 655, 659, 662, 672, 673, 675, 677, 683, 690, 694, 699, 709, 713, 719–721, 724, 728, 733, 740, 743, 748, 751, 756, 759, 768, 769, 775, 777, 779, 787, 790, 791, 795, 810, 812, 815, 821, 830, 840, (841), 842, 850–853, 857, 859–865, 873–876, 884, 886, 889, 892, 896, 897, 900
(*b*) Emulsion Systems. The above principles also apply for an emulsion system with the added advantage that the reaction medium is more homogeneous. In addition, emulsion polymerizations do not become unduly viscous	1, 2, 4, 9, 11, 12, 16, 29, 46, 48, 49, 53, 75, 91, 149, 150, 154, 226, 242–244, 252, 261, 271–275, 293, 352, 377, 384, 516, (517), 571, 592, 601, 607, 617, (618), 620, 644, 669, 691, 692, 716, 726, 727, 736, 762–765, 778, 802, 804, (805), 808, 828, 833,

at high conversions as do bulk and solution polymerizations. They are therefore attractive as grafting systems.	836, 846, (849), 866, 879, 880, 887
(*c*) Ionic Initiation. By the use of complexed anionic or cationic initiators graft copolymerization may be brought about by an ionic mechanism.	63–(65), 73, 127, 155, 365, 387, 424, (425), 442, 451, 493, 538, 580, 584, 658, 676, 695, 698, 710, 760, 817, (818), 819
2. Hydroperoxidation	
The introduction of hydroperoxide groups at random positions along the length of a polymer chain to form a multifunctional initiator has been used by many workers in the synthesis of graft copolymers. Graft copolymerization may be initiated by thermal or by redox activation of the hydroperoxidic groups. Homopolymerization of the second stage monomer also occurs when thermal initiation is used because of the nonpolymeric hydroxyl radicals.	
(*a*) Direct Oxidation. One of the simplest methods of obtaining hydroperoxide groups along a backbone polymer chain is by the direct oxidation of suitable sidegroups.	37, 58, 110, 133, (134), 181, 157, 158, 323, (324), 499, 519, 573–(575), 589, (590), 651–653, 684, 700, 732, 770, 806, 890, 891, 893, 894
(*b*) Ozonization. Ozonization, as the method of introducing hydroperoxide groups, has been found in some cases to be more efficient than air oxidation techniques.	87, 193, 194, 215–(220), 231, 296, (297), 361, 396, (397), 535, 564, 593, 613, 651, 652, 670, 737, 798, 799, 890, 899
3. Diazotization	
Other reactive groups besides the hydroperoxide type can be introduced into polymer chains and later decomposed in the presence of a vinyl monomer to yield graft copolymers. Thus nitration followed by diazotization and subsequent decomposition of the diazotized polymer yields radical sites which can initiate graft copolymerization. Similarly, nitrosation of a polymer followed by decomposition to yield macroradicals can be used for grafting reactions.	419, 527–530, 534–537, 630

(*continued*)

Method	References
4. Degradation	
(*a*) Thermal Degradation. The decomposition of thermally unstable groups on a polymeric backbone may be used to initiate graft copolymerization	233, (234), 411, 327, 389–(391), 482, 742, 744, 822, 885, 902
(*b*) Mechanical Degradation (Mastication). Under the influence of an applied stress scission of the carbon-carbon or other chemical bonds between atoms may occur within the backbone of a polymer macromolecule. This leads to the formation of macroradicals capable of initiating graft copolymerization	50, 88, 115, 116, 222, 270, 591, 603, (604), 626, 682, 685, 807, 887
5. Functional group reactions.	
(*a*) Condensation. Polymer molecules containing hydroxyl, carboxyl, amine, thiol, and certain ester groupings may be chemically linked together, to form graft copolymers, by the condensation type of reaction.	5, 8, 10, 14, 51, 74, 165–7, 176, 305, (306), 336, 412, 413, 551, 579, 587, 622, 667, 752–3
(*b*) Redox Initiation. This method of synthesis depends on the redox reaction of certain ceric salts (such as nitrate and sulfate) with organic reducing agents such as alcohols, thiols, glycols, aldehydes, and amines. If a polymeric reducing agent is employed and the oxidation conducted in the presence of a vinyl monomer, graft formation will occur. This technique yields relatively pure copolymers since the initiating sites are produced only on the backbone. A number of grafts have been prepared in aqueous solutions as well as in emulsion systems.	44, 140, (141), (142), 245, 265, 335, 357, 366, 531, 577, 665, 668, 708, 711, 715, 758, 800

APPENDIX VIII

Appendix VIII contains an index of the graft copolymers claimed in the patent abstracts of Appendixes II and III. The index has been divided into three parts.

Appendix VIIIA lists alphabetically graft copolymers for which both the polymer backbone and grafted side chain have been specifically defined.

Appendix VIIIB is an index of graft copolymers abstracted in appendixes II and III where either the backbone or the grafted side chain has *not* been specifically defined. e.g.,

poly(vinyl chloride-*g*-alkyl acrylate)

or

poly(α-olefin-*g*-methyl methacrylate)

Appendix VIIIC is a reference list to the patent abstracts where neither the backbone polymer nor the grafted side chain has been specifically defined, e.g.,

poly(esters-*g*-α-oelfins)

The following coding has been used throughout the index detailed in Appendixes VIIIA, VIIIB, and VIIIC.

(h) e.g., poly(ethylene(h)-*g*-styrene)

The small "h" in parentheses following a monomeric unit indicates that homolgs of the series may also be claimed.

*, e.g., poly(butadiene * -*g*-styrene)

The asterisk signifies that *minor* amounts of a copolymer of butadiene may also be claimed as the backbone polymer

(sub), e.g., poly(vinyl chloride-*g*-acrylamide(sub))

The abbreviation "sub" in parentheses following a monomeric unit signifies that substituted products of that monomer may also be covered by the claim.

C_{2-18}, e.g., poly(styrene-*g*-alkyl acrylate C_{2-18})

The abbreviation C_{2-18} signifies that the alkyl chain of the acrylate unit may contain from 2 to 18 carbon atoms.

The use of this form of nomenclature was found necessary due to the limited amount of information that could be obtained from a short abstract. In most cases time did not permit an examination of the complete specification.

APPENDIX VIIIA

Graft Copolymer Index

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Carboxymethyl cellulose-*g*-poly(butadiene) 110
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Poly[(styrene-*co*-maleic anhydride)-*g*-epichlorohydrin] 8
Poly[(styrene-*co*-maleic anhydride)-*g*-3,4,-epoxy-1-butene] 8
Poly[(styrene-*co*-maleic anhydride)-*g*-ethylene oxide] 8

Poly[(styrene-*co*-maleic anhydride)-*g*-phenylene oxide] 8
Poly[(styrene-*co*-maleic anhydride)-*g*-propylene oxide] 8
Poly[(styrene-*co*-*N*-methacryl caprolactam)-*g*-*ε*-caprolactam] 539, 540
Poly(styrene-*g*-methacrylic acid) 115
Poly[(styrene-*co*-methacrylic acid-*co*-divinylbenzene)-*g*-(butadiene-*co*-4-vinylpyridine)] 76
Poly[(styrene-*co*-methacrylic acid-*co*-divinylbenzene)-*g*-(styrene-*co*-methacrolein)] 76
Poly[(styrene-*co*-methylacrylic acid)-*g*-ethylene oxide] 8
Poly(styrene-*g*-methyl acrylate) 37
Poly(styrene-*g*-methyl methacrylate) 115, 170, 171, 387, 399, 739
Poly[(styrene-*co*-monobromostyrene)-*g*-ethylene] 580
Poly(styrene-*g*-propylene) 442
Poly(styrene *-*g*-styrene*) 200, 213
Poly[styrene-*g*-(styrene-*co*-acrylonitrile)] 213
Poly(styrene-*g*-vinyl acetate) 37
Poly(styrene-*g*-vinylcarbazole) 170, 171
Poly(styrene-*g*-vinyl chloride) 170, 171
Poly(styrene-*g*-vinylidene chloride) 193
Poly[(styrene-*co*-*α*-vinylnaphthalene)-*g*-acrylonitrile] 89, 90
Poly[(styrene-*co*-*α*-vinyl naphthalene)-*g*-methyl methacrylate] 89, 90
Poly[(styrene-*co*-*α*-vinyl naphthalene)-*g*-styrene-*co*-acrylonitrile] 89, 90
Poly[(styrne-*co*-*α*-vinyl naphthalene)-*g*-vinyl acetate] 89, 90
Poly(styrene-*g*-*N*-vinyl-2-pyridine) 739
Poly[(styrene-*co*-4-pyridine-*co*-divinylbenzene)-*g*-urea formaldehyde] 76
Poly(styrene-*g*-*N*-vinylpyrrolidone) 193
Poly(tetrafluoroethylene-*g*-acrylonitrile) 102, 103, 104, 105.
Poly(tetrafluoroethylene-*g*-butadiene) 102, 103, 104, 105
Poly(tetrafluoroethylene-*g*-ethyl acrylate) 484
Poly(tetrafluoroethylene-*g*-isoprene) 102, 103, 104, 105, 298, 299, 300
Poly(tetrafluoroethylene-*g*-methyl methacrylate) 298, 299, 300, 348, 484
Poly(tetrafluoroethylene-*g*-styrene) 102, 103, 104, 105, 298, 299, 300, 348, 350
Poly[tetrafluoroethylene-*g*-(styrene-*co*-acrylic acid)] 670
Poly(tetrafluoroethylene *-*g*-tetrafluoroethylene*) 200, 201
Poly(tetrafluoroethylene-*g*-vinyl chloride) 102, 103, 104, 105
Poly(tetrafluoroethylene-*g*-vinylidene chloride) 102, 103, 104, 105
Poly[*N*,*N*,*N*′,*N*′-tetramethyl fumaramide-*g*-(acrylonitrile-*co*-methyl acrylate-*g*-methyl acrylate)] 32
Poly(*N*,*N*,*N*′,*N*′-tetramethyl fumaramide-*g*-vinyl acetate-*g*-acrylonitrile) 32
Poly(tridecyl acrylate-*g*-vinyl chloride) 692, 693
Poly(trifluorochloroethylene-*g*-isoprene) 298, 299, 300, 348
Poly(trifluorochloroethylene-*g*-methyl methacrylate) 298, 299, 300, 348, 720
Poly(trifluorochloroethylene-*g*-styrene) 298, 299, 300, 348, 720
Poly(vinyl acetate-*g*-acrylonitrile) 15, 61
Poly[(vinyl acetate-*co*-acrylonitrile)-*g*-vinyl chloride] 120
Poly(vinyl acetate-*g*-ethylene) 3, 6, 263, 264
Poly[(vinyl acetate-*co*-isopropenyl acetate)-*g*-acrylonitrile] 19
Poly[(vinyl acetate-*co*-isopropenyl acetate-*g*-epichlorohydrin] 8
Poly[(vinyl acetate-*co*-isopropenyl acetate)-*g*-epoxy-1-butene] 8

Poly[(vinyl acetate-*co*-isopropenyl acetate)-*g*-ethylene oxide] 8
Poly[(vinyl acetate-*co*-isopropenyl acetate)-*g*-phenylene oxide] 8
Poly[(vinyl acetate-*co*-isopropenyl acetate)-*g*-propylene oxide] 8
Poly[(vinyl acetate-*co*-methacrylamide)-*g*-acrylonitrile] 3,4
Poly(vinyl acetate-*g*-methacrylic acid) 115
Poly[vinyl acetate-*g*-*N*-methyl methacrylamide-*g*-(acrylonitrile-*co*-*N*-methyl methacrylamide)] 32
Poly(vinyl acetate-*g*-methyl methacrylate) 115
Poly[(vinyl acetate-*co*-methyl methacrylate)-*g*-acrylonitrile] 19
Poly(vinyl acetate-*g*-styrene) 25, 115, 685
Poly[(vinyl acetate-*co*-vinyl alcohol)-*g*-acrylonitrile] 16
Poly[(vinyl acetate-*co*-vinyl alcohol-*g*-vinyl chloride(*)] 151
Poly(vinyl acetate-*g*-vinylidene chloride) 120
Poly[(vinyl acetate-*co*-*N*-vinyl phthalimide)-*g*-(acrylonitrile-*co*-*N*-vinyl succinimide)] 31
Poly(vinyl alcohol-*g*-acrylamide) 140, 141, 142, 371
Poly(vinyl alcohol-*g*-acrylonitrile*) 132, 140, 141, 142
Poly(vinyl alcohol-*g*-acrylonitrile) 20, 21, 28, 35, 45, 283, 284, 286, 371
Poly(vinyl alcohol-*g*-ethyl acrylate) 452
Poly[vinyl alcohol-*g*-(ethyl acrylate-*co*-acrylonitrile)] 452
Poly(vinyl alcohol-*g*-ethylene) 3, 6
Poly(vinyl alcohol-*g*-butyl acrylate) 452
Poly[vinyl alcohol-*g*-(butyl acrylate-*co*-acrylonitrile)] 452
Poly(vinyl alcohol-*g*-methacrylic acid) 115
Poly(vinyl alcohol-*g*-methyl acrylate) 140, 141, 142
Poly(vinyl alcohol-*g*-styrene) 78, 79, 140, 141, 142, 441, 600
Poly(vinyl alcohol-*g*-vinyl acetate) 75, 283, 284, 285, 286,
Poly(vinyl alcohol-*g*-vinyl chloride) 151, 736, 778
Poly(vinyl butyral-*g*-diisobutene) 115
Poly(vinyl butyral-*g*-methacrylic acid) 115
Poly(vinyl butyral-*g*-methyl methacrylate) 115
Poly(vinyl butyral-*g*-α-methylstyrene) 677
Poly(vinyl butyral-*g*-styrene) 115
Poly(vinyl butyral-*g*-vinyl acetate) 115
Poly(vinyl chloride-*g*-acrylamide) 95, 96, 97
Poly(vinyl chloride-*g*-acrylic acid) 411, 655, 720
Poly(vinyl chloride *-*g*-acrylonitrile*) 143, 144, 145
Poly(vinyl chloride-*g*-acrylonitrile) 29, 95, 96, 97, 102, 103, 104, 105, 170, 171, 211, 212, 225, 411, 655, 699
Poly[vinyl chloride-*g*-(acrylonitrile-*co*-butadene-*co*-divinylbenzene)] 767
Poly[vinyl chloride-*g*-(acrylonitrile-*co*-styrene)] 594, 595, 596, 844, 845
Poly(vinyl chloride-*g*-butadiene) 102, 103, 104, 105, 170, 171, 411, 495, 496, 546, 547, 591, 607, 727
Poly[vinyl chloride *-*g*-(butadiene-*co*-acrylonitrile)] 586, 686, 714
Poly[vinyl chloride *-*g*-(butadiene-*co*-methyl methacrylate)] 586, 686, 714
Poly[vinyl chloride-*g*-(butadiene-*co*-acrylonitrile-*co*-acrylic acid(h)] 377
Poly(vinyl chloride-*g*-chloroprene) 270
Poly(vinyl chloride-*g*-diallyl sebacate) 182
Poly(vinyl chloride-*g*-ethyl acrylate) 115

Poly(vinyl chloride-*g*-ethylene) 170, 171, 263, 264
Poly(vinyl chloride-*g*-ethylene(Cl)) 626
Poly(vinyl chloride-*g*-ethyl glycol dimethacrylate) 13
Poly(vinyl chloride-*g*-2-ethyl hexyl acrylate) 752, 753
Poly(vinyl chloride-*g*-ethyl methacrylate) 115
Poly(vinyl chloride-*g*-glycidyl acrylate) 525
Poly(vinyl chloride-*g*-hexafluoropropene) 159, 160
Poly(vinyl chloride *-*g*-isoprene) 727
Poly(vinyl chloride-*g*-isoprene) 102, 103, 104, 105
Poly(vinyl chloride-*g*-methacrylic acid) 411
Poly(vinyl chloride-*g*-methyl acrylate) 227
Poly(vinyl chloride-*g*-methyl methacrylate) 106, 115, 170, 171, 225, 720, 766
Poly(vinyl chloride-*g*-α-methyl styrene) 677
Poly(vinyl chloride-*g*-*n*-butyl acrylate) 115
Poly(vinyl chloride-*g*-perfluorocyclobutene) 159, 160
Poly(vinyl chloride-*g*-styrene) 102, 103, 104, 105, 106, 225, 411, 720, 766
Poly[vinyl chloride-*g*-(styrene-*co*-vinyl acetate)] 581
Poly(vinyl chloride-*g*-tetrafluoroethylene) 159, 160
Poly(vinyl chloride-*g*-triallyl cyanurate) 182
Poly(vinyl chloride-*g*-vinyl acetate) 411, 655
Poly[vinyl chloride-*g*-(vinyl acetate-*co*-vinyl acetate)] 411
Poly[(vinyl chloride-*co*-vinyl acetate)-*g*-butadiene] 614
Poly[(vinyl chloride-*co*-vinyl acetate)-*g*-ethylene glycol dimethacrylate] 230
Poly(vinyl chloride-*g*-vinylcarbazole) 170, 171
Poly(vinyl chloride-*g*-vinylidene chloride) 102, 103, 104, 105, 106, 411
Poly[(vinyl chloride-*co*-vinylidene chloride)-*g*-acrylonitrile] 288, 290, 721
Poly[(vinyl chloride-*co*-vinylidene chloride)-*g*-butadiene] 411
Poly[(vinyl chloride-*co*-vinylidene chloride)-*g*-ethyl acrylate] 289, 291, 721
Poly[(vinyl chloride-*co*-vinylidene chloride-*g*-methyl acrylate] 227
Poly(vinyl chloride-*g*-2-vinylpyridine) 655
Poly(vinyl chloride-*g*-*N*-vinyl-2-pyrrolidone) 655
Poly(vinyl chloride-*g*-vinyl stearate) 225
Poly[(*N*-vinyl-*N*-chloroacetamide-*co*-*N*-vinyl phthalimide)-*g*-acrylonitrile] 31
Poly(vinyl crotonal-*g*-acrylonitrile) 7
Poly(vinyl crotonal-*g*-ethyl acrylate) 7
Poly(vinyl crotonal-*g*-methallyl chloride) 7
Poly(vinylcrotonal-*g*-methyl acrylate) 7
Poly(vinyl crotonal-*g*-vinyl acetate) 7
Poly(*N*-vinyl diacetamide-*g*-acrylonitrile) 31
Poly[(vinyl diacetamide-*co*-acrylonitrile)-*g*-acrylonitrile] 31
Poly[*N*-vinyl diacetamide-*g*-(acrylonitrile-*co*-*N*-vinyl diacetamide)] 31
Poly[(vinyl ethyl ether-*co*-maleic anhydride)-*g*-ethylene oxide] 8
Poly(vinyl ethyl ether-*g*-vinyl acetate) 523
Poly[(vinyl ethyl hexyl ether-*co*-maleic anhydride)-*g*-epichlorohydrin] 8
Poly[(vinyl ethyl hexyl ether-*co*-maleic anhydride)-*g*-epoxy-*1*-butene] 8
Poly[(vinyl ethyl hexyl ether-*co*-maleic anhydride)-*g*-ethylene oxide] 8
Poly[(vinyl ethyl hexyl ether-*co*-maleic anhydride)-*g*-phenyl ethylene oxide] 8
Poly[(vinyl ethyl hexyl ether-*co*-maleic anhydride)-*g*-propylene oxide] 8

Poly[vinyl fluoride-*g*-(butadiene-*co*-sulfur dioxide)] 561, 562, 563
Poly[vinyl fluoride-*g*-(ethylene-*co*-sulfur dioxide)] 561, 562, 563
Poly(vinyl fluoride-*g*-methyl methacrylate) 106
Poly(vinyl fluoride-*g*-styrene) 106
Poly(vinyl fluoride-*g*-vinylidene chloride) 106
Poly(vinyl formal-*g*-acrylonitrile) 26
Poly(vinyl formal-*g*-methyl methacrylate) 115
Poly(vinyl formal-*g*-styrene) 115
Poly(vinyl formal-*g*-vinyl acetate) 115
Poly(vinylidene chloride-*g*-acrylamide) 37
Poly(vinylidene chloride-*g*-acrylonitrile) 29
Poly[vinylidene chloride-*g*-(acrylonitrile-*co*-styrene)] 596
Poly(vinylidene chloride-*g*-ethylene) 3, 6
Poly(vinylidene chloride-*g*-2-ethyl hexyl acrylate) 752, 753
Poly(vinylidene chloride-*g*-glycidyl acrylate) 525
Poly(vinylidene chloride-*g*-hexafluoropropene) 159, 160
Poly[(vinylidene chloride-*co*-methyl acrylate)-*g*-acrylonitrile] 29
Poly(vinylidene chloride-*g*-methyl methacrylate) 115
Poly(vinylidene chloride-*g*-parafluorocyclobutene) 159, 160
Poly(vinylidene chloride-*g*-styrene) 37
Poly(vinylidene chloride-*g*-tetrafluoroethylene) 159, 160
Poly(vinylidene chloride-*g*-vinyl acetate) 37
Poly[(vinylidene chloride-*co*-vinyl chloride)-*g*-acrylonitrile] 29
Poly[(vinyl isopropenyl ether-*co*-maleic anhydride)-*g*-ethylene oxide) 8
Poly(vinyl lactam-*g*-acrylamide) 393
Poly[vinyl lactam(h)-*g*-(ethylene glycol(h)-*co*-methyl methacrylate(h)-*co*-styrene sulfonate)] 314, 315, 316, 317, 318, 319, 320
Poly(vinyl lactam-*g*-methacrylamide) 393
Poly(*N*-vinyl lactam(h)-*g*-styrene) 616, 618
Poly(vinyl laurate-*g*-ethylene oxide) 10
Poly[(*N*-vinyl-*N*-methyl acetamide-*co*-acrylonitrile)-*g*-acrylonitrile] 31
Poly[(*N*-vinyl-*N*-methyl acetamide-*co*-acrylonitrile)-*g*-(acrylonitrile-*co*-methyl acrylate)] 31
Poly[(*N*-vinyl-*N*-methyl acetamide-*co*-dimethyl fumarate)-*g*-acrylonitrile] 31
Poly(*N*-vinyl-*N*-methyl acetamide-*g*-vinyl acetate) 795
Poly[(*N*-vinyl-*N*-methyl acetamide-*co*-*N*-vinyl phthalimide)-*g*-(acrylonitrile-*co*-*N*-methyl acrylamide)] 31
Poly(*N*-vinyl-3-morpholinone-*g*-acrylonitrile) 545
Poly[(*N*-vinyl-3-morpholinone-*co*-*N*-vinylpyridine)-*g*-amino-ethyl acrylate] 514
Poly(α-vinylnaphthalene-*g*-acrylonitrile) 89, 90
Poly[(*N*-vinyl-2-oxazolidinone-*co*-*N*-vinyl lactam)-*g*-acrylamide] 541
Poly[(*N*-vinyl-2-oxazolidinone-*co*-*N*-vinyl lactam)-*g*-amino-ethyl acrylate] 515
Poly[(*N*-vinyl-2-oxazolidinone-co-*N*-vinyl lactam)-*g*-methacrylamide] 541
Poly(vinyl palmitate-*g*-ethylene oxide) 10
Poly(vinylpyridine-*g*-acrylamide) 371
Poly[(vinylpyridine-*co*-acrylic acid)-*g*-acrylonitrile*] 109, 191, 192
Poly(vinylpyridine-*g*-acrylonitrile) 67, 371, 389, 392
Poly[(vinylpyridine-*co*-acrylonitrile)-*g*-acrylonitrile] 392

Poly(*N*-vinylpyrrolidone-*g*-acrylonitrile) 20, 21, 35, 132, 146, 224
Poly[N-vinylpyrrolidone-*g*-(acrylonitrile-*co*-methyl acrylate)] 146
Poly[*N*-vinylpyrrolidone-*g*-(acrylonitrile-*co*-vinyl acetate)] 146
Poly(*N*-vinylpyrrolidone-*g*-(acrylonitrile-*co*-vinylpyridine)] 146
Poly[*N*-vinylpyrrolidone(h)-*g*-(ethylene glycol(h)-*co*-methyl methacrylate(h)-*co*-styrene sulfonate)] 314, 315, 316, 317, 318, 319, 320
Poly(*N*-vinylpyrrolidone-*g*-methacrylic acid) 115
Poly(*N*-vinylpyrrolidone-*g*-methyl methacrylate) 878
Poly(*N*-vinylpyrrolidone-*g*-vinyl acetate) 725, 733
Poly[(*N*-vinylpyrrolidone-*co*-vinyl acetate)-*g*-acrylonitrile*] 132
Poly[*N*-vinylpyrrolidone-*g*-vinyl chloride] 769
Poly(vinyl stearate-*g*-ethylene oxide) 10
Poly(*N*-vinyl succinimide-*g*-acrylonitrile) 31
Poly[*N*-vinyl succinimide-*g*-(acrylonitrile-*co*-methyl fumaramate)] 31
Poly [*N*-vinyl succinimide-*g*-(acrylonitrile-*co*-vinyl acetate)] 31
Poly[(vinyl toluene-*co*-butadiene)-*g*-acrylonitrile] 147, 148
Poly[(vinyl toluene-*co*-butadiene)-*g*-methyl acrylate] 147, 148
Poly[(vinyl toluene-*co*-butadiene)-*g*-propylene] 147, 148
Poly[(vinyl toluene-*co*-butadiene)-*g*-vinyl chloride] 147, 148
Poly[(vinyl toluene-*co*-divinylbenzene-*co*-acrylonitrile)-*g*-ethylene] 147, 148
Protein-*g*-poly(acrylonitrile) 110, 641, 642, 643, 694, 792, 793
Protein-*g*-poly(butadiene) 110
Protein-*g*-poly(methyl acrylate-*co*-butyl acrylate) 690
Protein-*g*-poly(styrene) 110

Rayon-*g*-poly(acrylonitrile) 519, 520
Rayon-*g*-poly(styrene-*co*-acrylonitrile) 691
run-Congo copal-*g*-poly(methacrylic acid) 115
run-Congo copal-*g*-poly(methyl methacrylate) 115

Shellac-*g*-poly(diisobutene) 115
Shellac-*g*-poly(methyl methacrylate) 115
Shellac-*g*-poly(styrene) 115
Shellac-*g*-poly(vinyl acetate) 115
Starch-*g*-poly(acrylamide) 371
Starch-*g*-poly(acrylonitrile) 20, 21, 35, 205, 206, 207, 208, 371
Starch-*g*-poly(acrylonitrile-*co*-butadiene) 110
Starch-*g*-poly(butadiene) 205, 206, 207, 208
Starch-*g*-poly(butadiene-*co*-styrene) 110
Starch-*g*-poly(butyl acrylate) 452
Starch-*g*-poly(butyl acrylate-*co*-acrylonitrile) 452
Starch-*g*-poly(ethyl acrylate) 452
Starch-*g*-poly(ethyl acrylate-*co*-acrylonitrile) 452
Starch-*g*-poly(isoprene) 205, 206, 207, 208
Starch-*g*-poly(methacrylamide) 205, 206, 207, 208
Starch-*g*-poly(methyl methacrylate) 205, 206, 207, 208
Starch-*g*-poly(styrene) 205, 206, 207, 208, 453
Starch-*g*-poly(styrene-*co*-butadiene) 110
Starch-*g*-poly(vinyl acetate) 453
Starch methyl ether-*g*-poly(acrylonitrile) 20

Wool-*g*-poly(acrylamide(h)) 307, 308, 309
Wool-*g*-poly(acrylic acid(h)) 307, 308, 309
Wool-*g*-poly(acrylonitrile) 110
Wool-*g*-poly(butadiene) 110
Wool-*g*-poly(carbonate) 559
Wool-*g*-poly(styrene) 110, 600
Wool-*g*-poly(vinylpyridine(h)) 307, 308, 309
Wool-*g*-poly(vinylpyrrolidone(h)) 307, 308, 309
Wool-*g*-poly(urethan) 559

APPENDIX VIIIB

Graft Copolymers Abstracted in Appendixes II and III Where Either the Backbone or the Grafted Side Chain Has Not Been Specifically Defined

Poly(acetal-*g*-acrylamide) 140, 141, 142, 302, 303
Poly(acetal-*g*-acrylonitrile) 140, 141, 142
Poly(acetal-*g*-ethyl acrylate) 751
Poly(acetal-*g*-methyl acrylate) 140, 141, 142
Poly(acetal-*g*-styrene) 140, 141, 142
Poly(acetal-*g*-trioxane) 702
Poly(acetal(h)-*g*-*N*-vinylpyrrolidone) 302, 303
Poly[acrylamide(h)-*g*-alkyl acrylate C1-8] 494
Poly(acrylonitrile-*g*-alkenyl aromatic polyglycol ether) 347
Poly(acrylonitrile-*g*-aminated alkenyl aromatic monomer) 347
Poly(acrylonitrile-*g*-aminated ethyl acrylate) 347
Poly(acrylonitrile-*g*-aminated methyl methacrylate) 347
Poly(acrylonitrile(h)-*g*-dibasic unsaturated acid(h) or anhydride(h)] 187, 188, 189
Poly(acrylonitrile-*g*-dimethyl amino ethyl acrylate) 345
Poly(acrylonitrile-*g*-α-olefin) 184, 185, 186
Poly(acrylonitrile-*g*-sulfonated alkenyl aromatic monomer) 347
Poly(acrylonitrile-*g*-sulfonated olefin) 347
Poly[(acrylonitrile-*co*-sulfonic acid)-*g*-acrylonitrile*] 132
Poly(acrylonitrile-*g*-*N*-vinyl cyclic carbamate) 388
Poly(acrylonitrile-*g*-*N*-vinyl heterocylic) 645
Poly(acrylonitrile-*g*-vinyl monomer) 184, 185, 186, 655
Poly(acrylonitrile-*g*-*N*-vinyl-2-oxazolidine) 339
Poly(acrylate(h)-*g*-acrylic acid (h)) 187, 188, 189, 190
Poly(acrylate(h)-*g*-acrylonitrile) 655
Poly(acrylate(h)-*g*-dibasic unsaturated acid (h) or anhydride(h)] 187, 188, 189, 190
Poly(acrylate(h)-*g*-vinyl monomer) 655, 768
Poly(acrylic acid-*g*-amino acid) 5
Poly(aldehyde-*g*-acrylamide) 140, 141, 142
Poly(aldehyde-*g*-acrylonitrile) 140, 141, 142
Poly(aldehyde-*g*-methyl acrylate) 140, 141, 142
Poly(aldehyde-*g*-styrene) 140, 141, 142

Poly(aldehyde-*g*-vinyl monomer) 530
Poly(alkenyl carbonamide-*g*-acrylonitrile) 18
Poly[(alkenyl carbonamides-*co*-*α*-olefins)-*g*-acrylonitrile] 18
Poly(*N*-alkyl acrylamide-*g*-acrylonitrile) 54, 55, 56
Poly(alkyl acrylate-*g*-butadiene) 812
Poly(alkyl acrylate C_{2-18}-*g*-methyl methacrylate) 550, 895
Poly(alkyl acrylate*-*g*-styrene) 685
Poly(alkyl acrylates-*g*-vinyl chloride) 53
Poly[alkyl acrylate-*g*-(vinyl chloride-*co*-vinylidene chloride)] 80, 83, 84
Poly(alkylene glycol(h)-*g*-acrylate *(h)) 378
Poly(alkylene glycol(h)-*g*-acrylonitrile) 521, 522
Poly(alkylene glycol-*g*-acrylic acid ester) 427
Poly(alkylene glycol(h)-*g*-methacrylate *(h)) 378
Poly(alkylene glycol(h)-*g*-*α*-olefin) 526
Poly(alkylene glycol (h)-*g*-vinyl ester*) 378, 426
Poly(alkylene glycol (h)-*g*-vinyl monomer) 524, 669
Poly(alkyl methacrylate (h)-*g*-acrylate(h)) 373, 374, 375
Poly(alkyl methacrylate (h)-*g*-acrylic acid(h)) 373, 374, 375
Poly(alkyl methacrylate(h)-*g*-acrylonitrile(h)) 373, 374, 375
Poly(alkyl methacrylate(h)-*g*-methacrylate(h)) 373, 374, 375
Poly(alkyl methacrylate(h)-*g*-methacrylic acid(h)) 373, 374, 375
Poly(alkyl methacrylate(h)-*g*-methacrylonitrile(h)) 373, 374, 375
Poly(alkyl methacrylate *-*g*-styrene) 685
Poly(alkyl methacrylate(h)-*g*-thioacrylate) 373, 374, 375
Poly(alkylene oxide-*g*-acrylic acid ester) 427
Poly(allyl ester-*g*-acrylonitrile) 19
Poly(amide-*g*-acrylic acid(h)) 165, 166, 167, 698, 758
Poly(amide-*g*-acrylonitrile) 170, 171
Poly(amide-*g*-butadiene) 102, 103, 104, 105, 170, 171
Poly(amide-*g*-ethylene) 170, 171
Poly(amide-*g*-hexafluoropropene) 159, 160
Poly(amide-*g*-isoprene) 102, 103, 104, 105
Poly(amide-*g*-methyl methacrylate) 170, 171, 195, 196, 197
Poly[amide-*g*-(*α*-olefin-*co*-sulfur dioxide)] 561, 562, 563
Poly(amide-*g*-perfluorocyclobutene) 159, 160
Poly(amide-*g*-styrene) 102, 103, 104, 105, 768
Poly(amide-*g*-styrene sulfonic acid) 164, 166, 167
Poly(amide-*g*-tetrafluoroethylene) 159, 160
Poly(amide-*g*-vinylcarbazole) 170, 171
Poly(amide-*g*-vinyl chloride) 102, 103, 104, 105, 170, 171
Poly(amide-*g*-vinylidene chloride) 102, 103, 104, 105, 768
Poly(amide-*g*-vinyl monomer) 529, 899, 902
Poly(amide-*g*-monomeric acid) 353
Poly(amide-*g*-*N*-vinyl-3-morpholinone) 434
Poly(amine-*g*-acrylamide) 140, 141, 142
Poly(amine-*g*-acrylonitrile) 140, 141, 142
Poly(amine-*g*-methyl acrylate) 140, 141, 142
Poly(amine-*g*-styrene) 140, 141, 142

Poly(butadiene(*h*)-*g*-acrylic acid ester(h)) 334
Poly[(butadiene-*co*-alkyl acrylate)-*g*-methyl methacrylate] 883
Poly[butadiene-*g*-(acrylate-*co*-acrylamide(sub))] 726
Poly[(butadiene-*co*-acrylonitrile)-*g*-alkyl acrylate] 351
Poly[(butadiene-*co*-acrylonitrile)-*g*-alkyl methacrylate] 351
Poly[(butadiene-*co*-acrylonitrile)-*g*-vinyl ester] 351
Poly(butadiene-*g*-alkyl acrylate), 351
Poly(butadiene-*g*-alkyl methacrylate) 351, 328, 329
Poly[butadiene-*g*-(alkyl methacrylate C1-3-*co*-α-methyl styrene(Cl))] 328
Poly(butadiene(h)-*g*-methacrylic acid ester (h)) 334
Poly[(butadiene-*co*-methyl isopropenyl ketone)-*g*-alkyl acrylate] 351
Poly[(butadiene-*co*-methyl isopropenyl ketone)-*g*-alkyl methacrylate] 351
Poly[(butadiene-*co*-methyl isopropenyl ketone)-*g*-vinyl ester] 351
Poly(butadiene *-*g*-α-olefin) 358
Poly[(butadiene-*co*-styrene)-*g*-alkyl acrolein (h)(469, 470
Poly[(butadiene-*co*-styrene)-*g*-alkyl acrylate] 351
Poly[(butadiene-*co*-styrene)-*g*-(alkyl acrylate-*co*-styrene)] 467
Poly[(butadiene-*co*-styrene)-*g*-alkyl methacrylate] 351
Poly[(butadiene-*co*-styrene)-g-divinyl monomer] 395
Poly[(butadiene-*co*-styrene)-*g*-vinyl ester] 351
Poly[(butadiene-*co*-styrene)-*g*-vinylidene monomer] 395
Poly[(butadiene-*co*-styrene)-*g*-vinyl monomer] 395, 468
Poly(butadiene-*g*-(sulfur dioxide-*co*-olefin) 24
Poly[(butadiene-*g*-vinyl aromatic compound (sub) (h)-*co*-vinyl acid (h)] 272, 273
Poly(butadiene-*g*-vinyl ester) 351
Poly(butyl rubber copolymers-*g*-methyl methacrylate) 549

Cellulose-*g*-poly(α-olefin) 184, 185, 186
Cellulose-*g*-poly(vinyl monomer) 184, 185, 186, 568, 615, 630, 671
Cellulose acetate-*g*-vinyl monomer 449, 450
Cellulose ester-*g*-poly(alkyl acrylate) 22

Poly(carbonate(h)-*g*-acrylamide) 302, 303
Poly(carbonate(h)-*g*-*N*-vinylpyrrolidone) 302, 303
Poly(chloropentadiene-*g*-(meth)acrylic ester(h)) 900
Poly(chloroprene *-*g*-α-olefin) 358

Poly(*N*,*N*-dialkyl acrylamide-*g*-acrylonitrile) 54, 55, 56
Poly[*N*,*N*-dialkyl acrylamide-*g*-(vinyl chloride-*co*-vinylidene chloride)] 81
Poly[*N*,*N*-dialkyl acrylamide-*g*-(vinyl chloride-*co*-vinylidene chloride-*co*-acrylonitrile)] 82
Poly(*N*,*N*-dialkyl acrylamide-*g*-(vinylchloride-*co*-vinylidene chloride-*co*-*N*,*N*-dialkylacrylamide)] 81
Poly[*N*,*N*-dialkyl acrylamide-*g*-(vinyl chloride-*co*-vinylidene chloride-*co*-methacrylonitrile)] 82
Poly[*N*,*N*-dialkyl acrylamide-*g*-(vinyl chloride-*co*-vinylidene chloride-*co*-methyl acrylate)] 82
Poly[*N*,*N*-dialkyl acrylamide-*g*-(vinyl chloride-*co*-vinylidene chloride-*co*-vinyl acetate)] 82

Poly(diene(h)-*g*-acrylonitrile) 194, 367, 368
Poly[(diene(h)-*co*-acrylonitrile)-*g*-unsaturated fatty acid] 822
Poly(diene(h)-*g*-diabasic unsaturated acid (h) or anhydride(h)) 187, 188, 189, 190
Poly(diene-*g*-methacrylonitrile) 367, 368
Poly(diene-*g*-*α*-olefin) 658
Poly(diene-*g*-styrene) 367, 368
Poly[diene-*g*-(styrene-*co*-acrylonitrile)] 786
Poly[(diene(h)-*co*-styrene)-*g*-unsaturated fatty acid] 822, 823, 824, 825
Poly(diene(h)-*g*-vinylidene chloride) 194
Poly[diene-*g*-(vinyl monomer-*co*-divinyl monomer)] 632
Poly(diene(h)-*g*-vinylpyrrolidone) 194
Poly(dimethyl butadiene *-*g*-*α*-olefin) 358

Poly(1,2-epoxy monomer-*g*-vinyl chloride) 572
Poly(1,2-epoxy monomer-*g*-vinylidene chloride) 572
Poly(ester-*g*-acrylamide) 799
Poly(ester-*g*-acrylonitrile) 102, 103, 104, 105
Poly(ester-*g*-acrylic acid) 799
Poly(ester-*g*-butadiene) 102, 103, 104, 105
Poly(ester-*g*-glycol methacrylate) 551
Poly(ester-*g*-isoprene) 102, 103, 104, 105
Poly(ester-*g*-maleic anhydride) 799
Poly(ester-*g*-methyl methacrylate) 195, 196, 197
Poly(ester-*g*-*α*-olefin) 341
Poly(ester-*g*-styrene) 102, 103, 104, 105, 768
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The subject index contains general references to the text, but for specific queries such as the radiation synthesis of a specific polymer or the physical properties of a species, reference should be made to the appropriate table. The reader should refer to Chapter I, Section 3, page 6, for the use of these tables.

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